Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 25-03 Pesticides in Soil

July 2025

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ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute Australia (NMIA). Support funding was provided by the Australian Government Department of Industry, Science and Resources.

I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMIA staff members in the planning, conduct and reporting of the study is acknowledged.

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NATA
WORLD RECOGNISED ACCREDITATION

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SUMMARY

AQA 25-03 Pesticides in Soil commenced in March 2025. Twenty-three laboratories enrolled to participate, and twenty-one submitted results.

Two soil samples were prepared by spiking soil with various pesticides.

Of a possible 231 results, a total of 122 numeric results (53%) were submitted. Thirty-five results were submitted as a 'less than' value (< *x*) or Not Reported (NR), and 74 results were submitted as Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were evaluated from the robust standard deviations of the participants' results.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

The outcomes of the study were assessed against the aims as follows:

- *Assess participants' ability to correctly identify pesticides in soil.*

Laboratories **3**, **5**, **10**, **16**, **17** and **21** reported results for all scored analytes.

Laboratories **1**, **10**, **12**, **14**, **16** and **19** reported false negatives ('less than' results where the assigned value was higher than their limit of reporting, or participants reporting NR; total of 24 results).

Eleven participants reported analytes that were not spiked into the test samples (total of 28 results).

- *Assess participants' capabilities to measure pesticides in soil.*

Of 104 *z*-scores, 90 (87%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Of 96 E_n-scores, 78 (81%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

- *Evaluate participants' methods for the measurement of pesticides in soil.*

Participants used a wide variety of methods, and no significant trend was observed for most analytes.

There may be a relationship between participants using SLE and diuron low recovery.

- *Develop the practical application of measurement uncertainty.*

Of 122 numeric results, 109 (89%) were reported with an associated evaluation of expanded uncertainty. The magnitude of these expanded uncertainties ranged from 2.1% to 100% of the reported value.

- *Produce materials that can be used in method validation and as control samples.*

The test samples produced for this study are homogeneous and are well characterised. Surplus of these samples is available for purchase and can be used for quality control and for method validation purposes.

1 INTRODUCTION

1.1 NMIA Proficiency Testing Program

The National Measurement Institute Australia (NMIA) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is the 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons'.[1] NMIA PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMIA offers studies in:

- pesticide residues in soil, water, fruit, vegetables and herbs;
- hydrocarbons, phenols and volatile organic compounds in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, biosolid, water, biota and food;
- controlled drug assay, drugs in wipes and clandestine laboratory; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess participants' ability to correctly identify pesticides in soil;
- assess participants' capabilities to measure pesticides in soil;
- evaluate participants' methods for the measurement of pesticides in soil;
- develop the practical application of measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

The choice of the test method was left to the participating laboratories.

1.3 Study Conduct

The conduct of NMIA PT studies is described in the NMIA Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMIA Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043 and The International Harmonized Protocol for The Proficiency Testing of Analytical Chemistry Laboratories.[1,4]

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043:2023 as a provider of PT schemes.[1] This study is within the scope of NMIA's accreditation.

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitations sent	10/03/2025
Samples sent	7/04/2025
Results due	19/05/2025
Interim Report	21/05/2025
Preliminary Report	22/05/2025

2.2 Participation and Laboratory Code

Twenty-three laboratories enrolled in this study, and all participants were assigned a confidential laboratory code number for this study. Of these, twenty-one submitted results.

2.3 Selection of Pesticides and Test Material Preparation

The pesticides and spiked values used in this study were selected with consideration to:

- a variety of pesticides amenable to gas and/or liquid chromatography; and
- the National Environment Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Soil was collected from a farm in New South Wales, Australia. The soil was spiked with various pesticides to obtain the mass fractions listed in Table 1.

Table 1 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty* (mg/kg)
S1	*p,p'*-DDT	0.301	0.015
	Diuron	1.01	0.05
	Endosulfan sulfate	0.753	0.038
	Glyphosate	1.51	0.08
	Lindane	0.121	0.006
	MCPA	0.606	0.030
S2	Atrazine	0.555	0.028
	Diazinon	0.453	0.023
	Fipronil	0.808	0.040
	Metsulfuron-methyl	0.759	0.038
	Triclopyr	1.21	0.06

*The uncertainty is an expanded uncertainty at approximately 95% confidence using a coverage factor of 2. It has been evaluated with consideration to contributions from the gravimetric and volumetric operations involved in spiking the samples, and the purity of the pesticide reference standards. Stability was not considered in the uncertainty budget and so the expanded uncertainty relates to the mass fraction of analyte at the time of spiking.

Further information on the preparation of the samples is given in Appendix 1.

2.4 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this PT study's samples. The samples were prepared, packaged, stored and dispatched using a process that has been demonstrated to

produce sufficiently homogeneous and stable samples in previous NMIA Pesticides in Soil PT studies.

Participants' results also gave no reason to question the homogeneity or transport stability of the samples (Appendix 2).

To further assess possible instability, the results returned by participants were compared to the spiked values. Assigned values for scored analytes were within 66% to 91% of the spiked values, which is similar to ratios observed in previous NMIA Pesticides in Soil PT studies (for example, as presented in PT Report AQA 16-04 Pesticides in Soil).[6]

2.5 Sample Storage, Dispatch and Receipt

The test samples were refrigerated at 4 °C prior to dispatch. Participants were sent 50 g spiked soil for each of Samples S1 and S2. The samples were packed in a polystyrene foam box with cooler bricks and sent by courier on 7 April 2025.

The following items were packaged with the samples:

- a letter which included a description of the test samples and instructions for participants; and
- a form for participants to return to confirm the receipt and condition of the samples.

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

2.6 Instructions to Participants

Participants were provided with a list of possible analytes spiked into Samples S1 and S2 (Table 2).

Table 2 List of Possible Analytes

2,4-D	p,p'-DDE	Fenitrothion	Metsulfuron-methyl
Aldrin	p,p'-DDT	Fenthion	Parathion
Atrazine	Total DDT	Fenvalerate	Parathion-methyl
Bifenthrin	Diazinon	Fipronil	Permethrin
cis-Chlordane	Dicamba	Glyphosate	Propiconazole
trans-Chlordane	Dieldrin	Heptachlor epoxide	Simazine
Total Chlordane	Diuron	Hexachlorobenzene	Tebuconazole
Chlorpyrifos	alpha-Endosulfan	Imidacloprid	Triclopyr
Cyfluthrin	beta-Endosulfan	Lindane	Trifluralin
Cypermethrin	Endosulfan sulfate	Malathion	
p,p'-DDD	Ethion	MCPA	

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.
- For each analyte in each sample report a single result on as received basis in units of mg/kg. This figure will be used in all statistical analysis in the study report.

- Report results as you would report to a client, i.e. corrected for recovery or not, according to your standard procedure, and applying the limit of reporting of the method used for analysis (no limit of reporting has been set for this study).
- For each analyte in each sample, report the associated expanded uncertainty in units of mg/kg (e.g. 0.50 ± 0.02 mg/kg).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Report any listed pesticide not tested with NT as the result.
- Report the basis of your uncertainty evaluation as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- Please complete the method details as requested in the Methodology sheet.
- Please return the completed results sheet by email (proficiency@measurement.gov.au).
- Return the completed results sheet by 5 May 2025. Late results may not be included in the study report.

The results due date was extended to 19 May 2025 due to delays with sample delivery to some participants and public holidays.

2.7 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 21 May 2025.

A Preliminary Report was emailed to all participants on 22 May 2025. This report included a summary of the results reported by participants, assigned values, performance coefficient of variations (PCVs), *z*-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses received are presented in Appendix 4.

3.2 Basis of Participants' Measurement Uncertainty Evaluation

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses received are presented in Table 3. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of Uncertainty Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
1	Standard uncertainty based on historical data k = 2	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/ CITAC Guide
2	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	Eurachem/ CITAC Guide
3	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported		CRM	ISO/GUM
4	Top Down - precision and estimates of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	CRM Instrument calibration	NMI Uncertainty Course
5	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	Recoveries of SS Standard purity	Eurachem/ CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/ CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Standard deviation from PT studies only		Nordtest Report TR537
		Control samples - RM / Ex PT Sample	CRM	
10	Coverage factor not reported			
11	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Duplicate analysis Instrument calibration	Recoveries of SS	ISO/GUM
12	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Duplicate analysis	Recoveries of SS	Eurachem/ CITAC Guide

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
		Precision	Method Bias	
13	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	ISO/GUM
14	Coverage factor not reported			
15	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS		ISO/GUM
16	k = 2	Control samples - SS Duplicate analysis Instrument calibration		Eurachem/ CITAC Guide
17	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Instrument calibration		ISO/GUM
18	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS		Eurachem/ CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS	Eurachem/ CITAC Guide
20	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Control samples	CRM	
21	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Duplicate analysis	Instrument calibration	
22	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - RM / Ex PT Sample Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
23	Measurement uncertainty based upon in-house historical data. Coverage factor not reported	Control samples - CRM		

* CRM = Certified Reference Material; RM = Reference Material; SS = Spiked Samples

3.3 Participants' Comments

Participants were invited to make comments on the samples, study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are presented in Table 4. Some comments may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments
13	S1	Glyphosate breakdown AMPA seen in sample at 0.02 mg/kg

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 15 with the summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max), minimum (Min), robust standard deviation (robust SD) and robust coefficient of variation (robust CV), and other estimates of analyte mass fraction. Bar charts of results and performance scores are presented in Figures 2 to 12, with an example chart with interpretation guide shown in Figure 1.

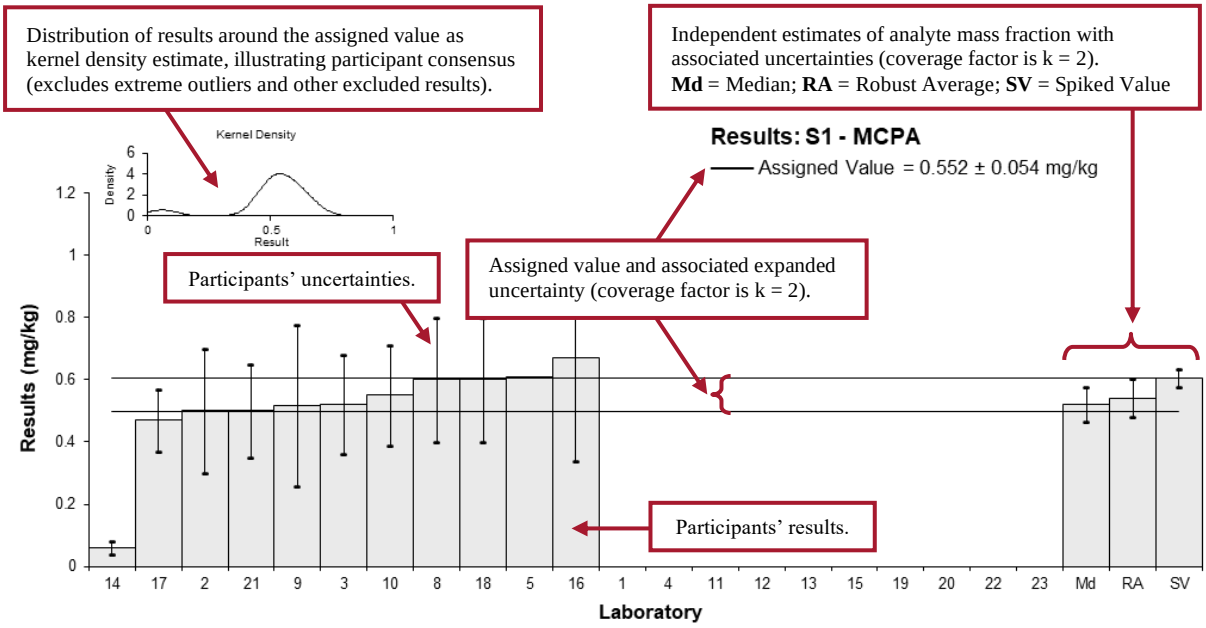


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Extreme outliers, if applicable, were obvious blunders, e.g. results with incorrect units, or for a different analyte or sample, and such results were removed before the calculation of all summary statistics.[3]

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic of a proficiency test item'.[1] In this PT study, the property is the mass fraction of the analytes in the samples. Assigned values were the robust averages of participants' results and the expanded uncertainties were evaluated from the associated robust SDs (Appendix 3).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated as described in ISO 13528.[7]

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants, given the levels of analytes present. The PCV is not the CV of participants' results. It is set by the study coordinator and is based on the mass fraction of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performance and can be compared from study to study.

4.6 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value (X) and the PCV, as presented in Equation 1.

$$\sigma = X \times PCV \qquad \textit{Equation 1}$$

4.7 z-Score

For each participant's result, a *z*-score is calculated according to Equation 2.

$$z = \frac{(\chi - X)}{\sigma} \qquad \textit{Equation 2}$$

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation for proficiency assessment from Equation 1

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result' (see Section 6.3 for more information).

For the absolute value of a *z*-score:

- $|z| \leq 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable; and
- $|z| \geq 3.0$ is unacceptable.

4.8 E_n-Score

The E_n-score is complementary to the *z*-score in assessment of laboratory performance. The E_n-score includes expanded uncertainty and is calculated according to Equation 3.

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi{}^2 + U_X{}^2}} \qquad \textit{Equation 3}$$

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

For the absolute value of an E_n-score:

- $|E_n| < 1.0$ is acceptable; and
- $|E_n| \geq 1.0$ is unacceptable.

4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[9]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[10]

5 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	*p*,*p*'-DDT
Unit	mg/kg

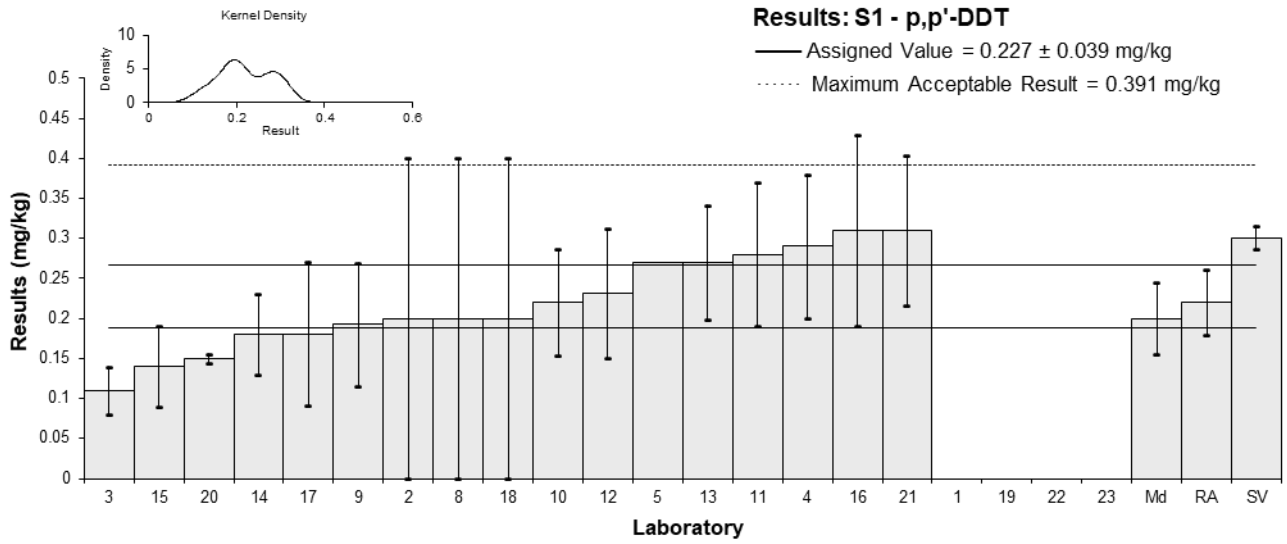
Participant Results

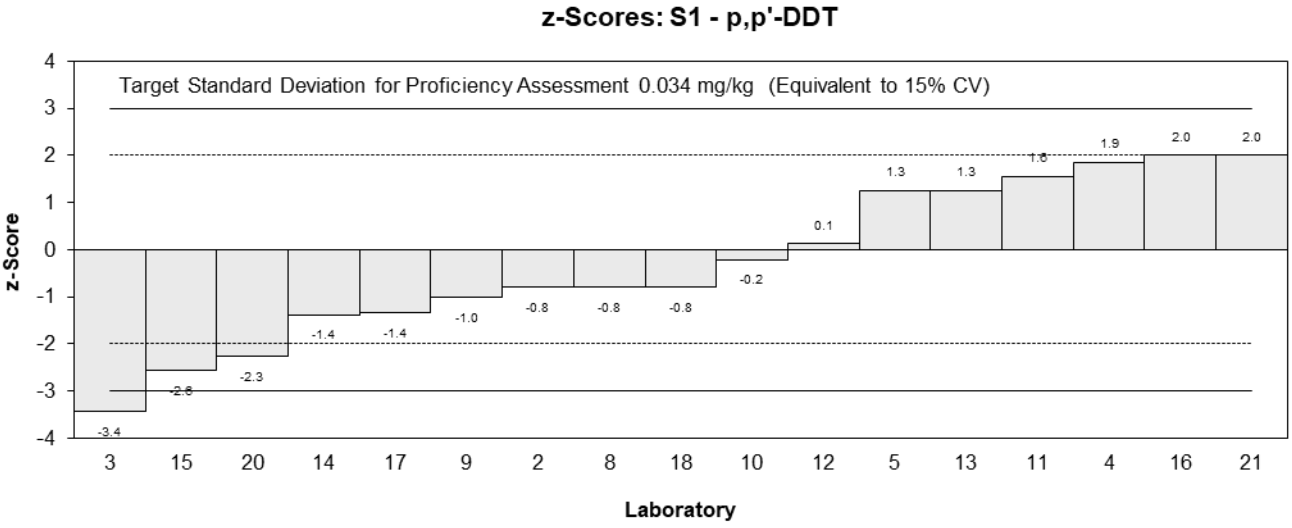
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.010	0.0061	NR		
2	0.2	0.2	80-120	-0.79	-0.13
3*	0.11	0.03	84	-3.44	-2.38
4	0.29	0.09	NR	1.85	0.64
5	0.27	NR	NR	1.26	1.10
8	0.2	0.2	80-120	-0.79	-0.13
9	0.1925	0.077	113	-1.01	-0.40
10	0.22	0.066	NR	-0.21	-0.09
11	0.28	0.09	106	1.56	0.54
12	0.231	0.081	96	0.12	0.04
13	0.27	0.072	96	1.26	0.53
14	0.18	0.05	NR	-1.38	-0.74
15	0.14	0.05	NR	-2.56	-1.37
16	0.31	0.12	111	2.00▼	
17	0.181	0.09	NR	-1.35	-0.47
18	0.2	0.2	NR	-0.79	-0.13
19	NR	NR	NR		
20	0.15	0.006	NR	-2.26	-1.95
21	0.31	0.093	NR	2.00▼	
22	NT	NT	NT		
23	<0.5	0.5	NR		

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.227	0.039
Spike Value	0.301	0.015
Robust Average	0.220	0.041
Max Acceptable Result	0.391	
Median	0.200	0.045
Mean	0.220	
N	17	
Max	0.31	
Min	0.11	
Robust SD	0.067	
Robust CV	31%	


Kernel Density
Density
Result
Results: S1 - p,p'-DDT
Assigned Value = 0.227 ± 0.039 mg/kg
Maximum Acceptable Result = 0.391 mg/kg
Results (mg/kg)
Laboratory
3 15 20 14 17 9 2 8 18 10 12 5 13 11 4 16 21 1 19 22 23 Md RA SV


z-Scores: S1 - p,p'-DDT
Target Standard Deviation for Proficiency Assessment 0.034 mg/kg (Equivalent to 15% CV)
z-Score
-3.4 -2.6 -2.3 -1.4 -1.4 -1.0 -0.8 -0.8 -0.8 -0.2 0.1 1.3 1.3 1.6 1.9 2.0 2.0
Laboratory
3 15 20 14 17 9 2 8 18 10 12 5 13 11 4 16 21

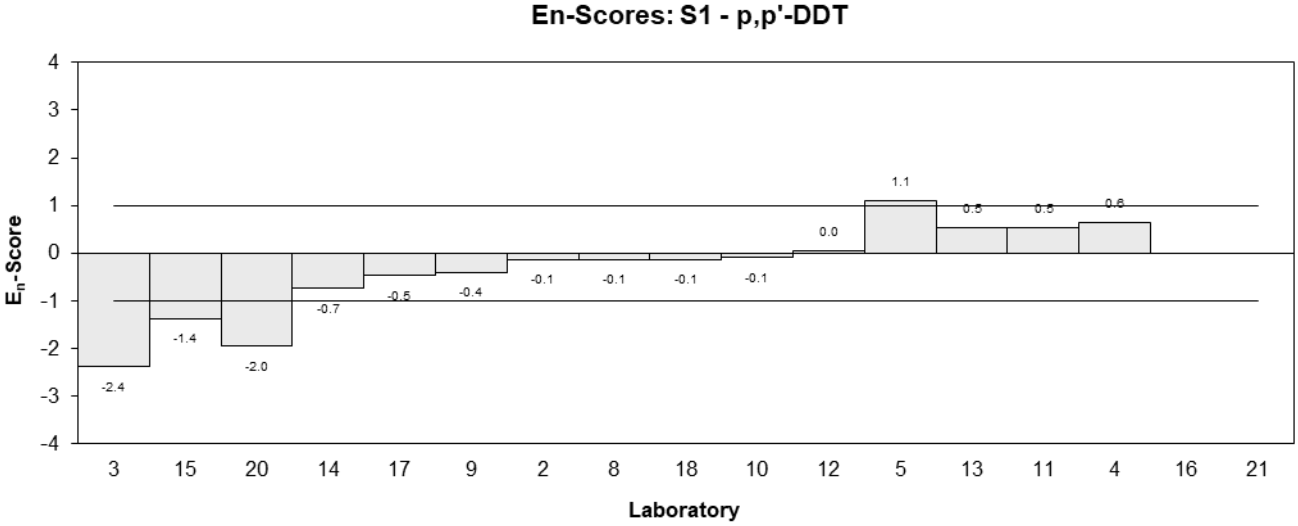

En-Scores: S1 - p,p'-DDT
En-Score
-2.4 -1.4 -2.0 -0.7 -0.5 -0.4 -0.1 -0.1 -0.1 -0.1 0.0 1.1 0.5 0.5 0.6
Laboratory
3 15 20 14 17 9 2 8 18 10 12 5 13 11 4 16 21

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Diuron
Unit	mg/kg

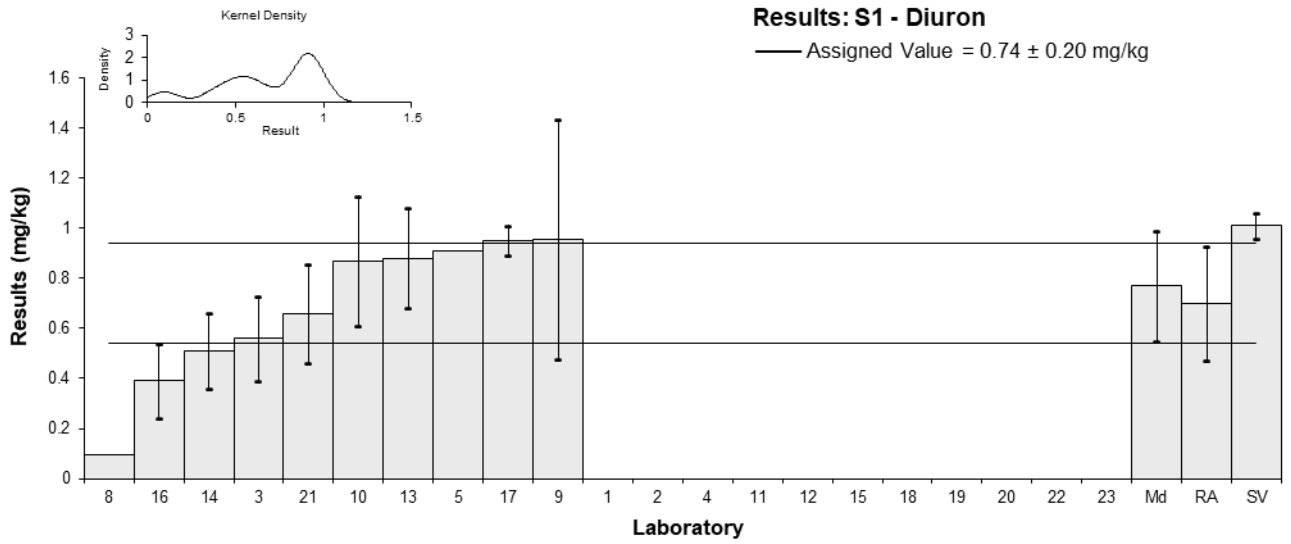
Participant Results

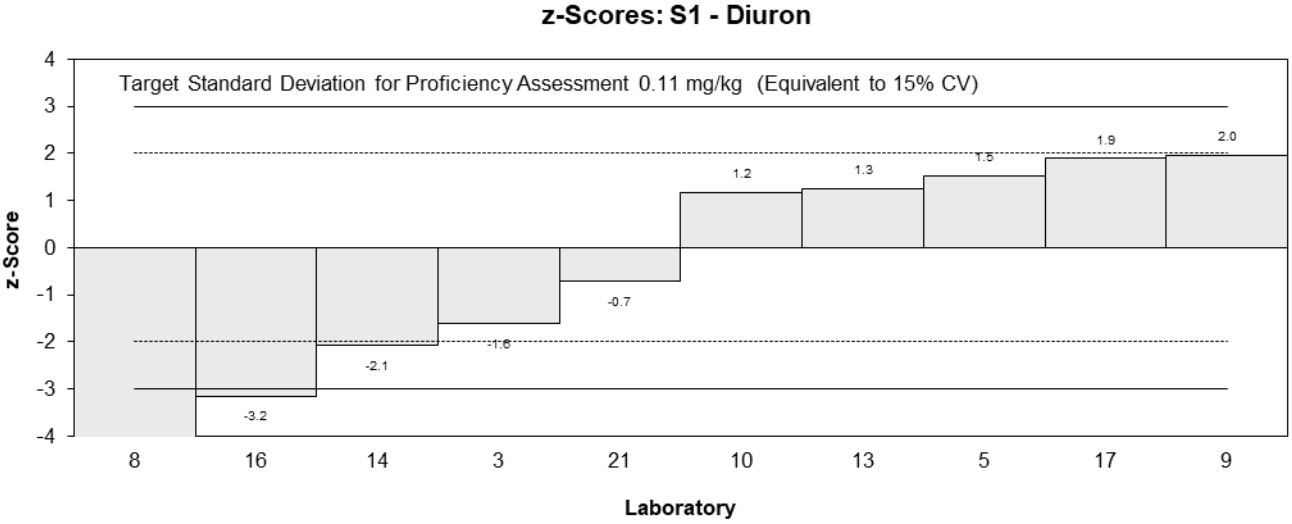
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.006	0.004	NR		
2	NT	NT	NT		
3	0.56	0.17	85	-1.62	-0.69
4	< 2	NR	NR		
5	0.91	NR	NR	1.53	0.85
8*	0.097	NR	80-120	-5.79	-3.22
9	0.956	0.478	102	1.95	0.42
10	0.87	0.26	NR	1.17	0.40
11	NT	NT	NT		
12	NT	NT	NT		
13	0.88	0.20	96	1.26	0.49
14	0.51	0.15	NR	-2.07	-0.92
15	NT	NT	NT		
16	0.39	0.15	76	-3.15	-1.40
17	0.95	0.06	NR	1.89	1.01
18	NT	NT	NT		
19	NR	NR	NR		
20	NT	NT	NT		
21	0.66	0.198	NR	-0.72	-0.28
22	NT	NT	NT		
23	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.74	0.20
Spike Value	1.01	0.05
Robust Average	0.70	0.23
Median	0.77	0.22
Mean	0.68	
N	10	
Max	0.956	
Min	0.097	
Robust SD	0.29	
Robust CV	41%	


Kernel Density
Density
Result
Results: S1 - Diuron
Assigned Value = 0.74 ± 0.20 mg/kg
Results (mg/kg)
Laboratory
8 16 14 3 21 10 13 5 17 9 1 2 4 11 12 15 18 19 20 22 23 Md RA SV


z-Scores: S1 - Diuron
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 16 14 3 21 10 13 5 17 9
-3.2
-3.2
-2.1
-1.6
-0.7
1.2
1.3
1.5
1.9
2.0

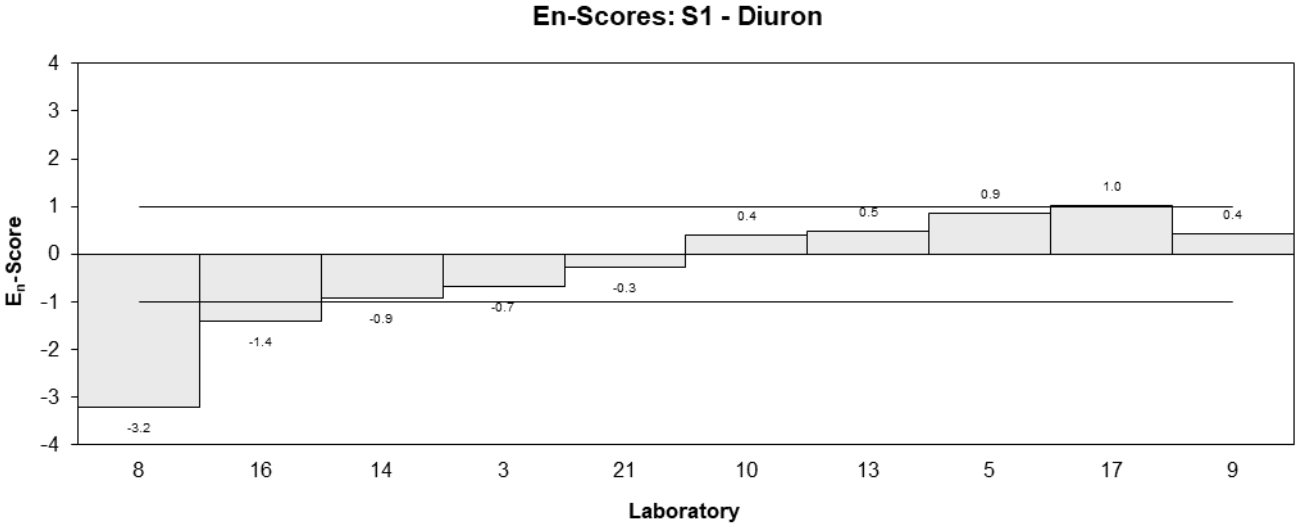

En-Scores: S1 - Diuron
En-Score
Laboratory
8 16 14 3 21 10 13 5 17 9
-3.2
-1.4
-0.9
-0.7
-0.3
0.4
0.5
0.9
1.0
0.4

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Endosulfan sulfate
Unit	mg/kg

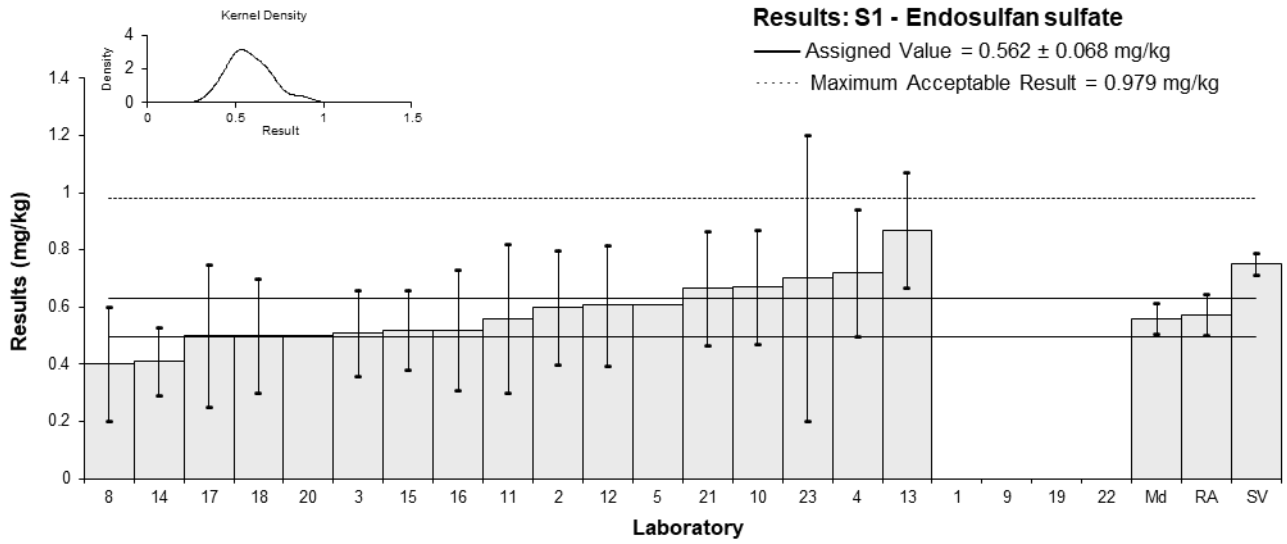
Participant Results

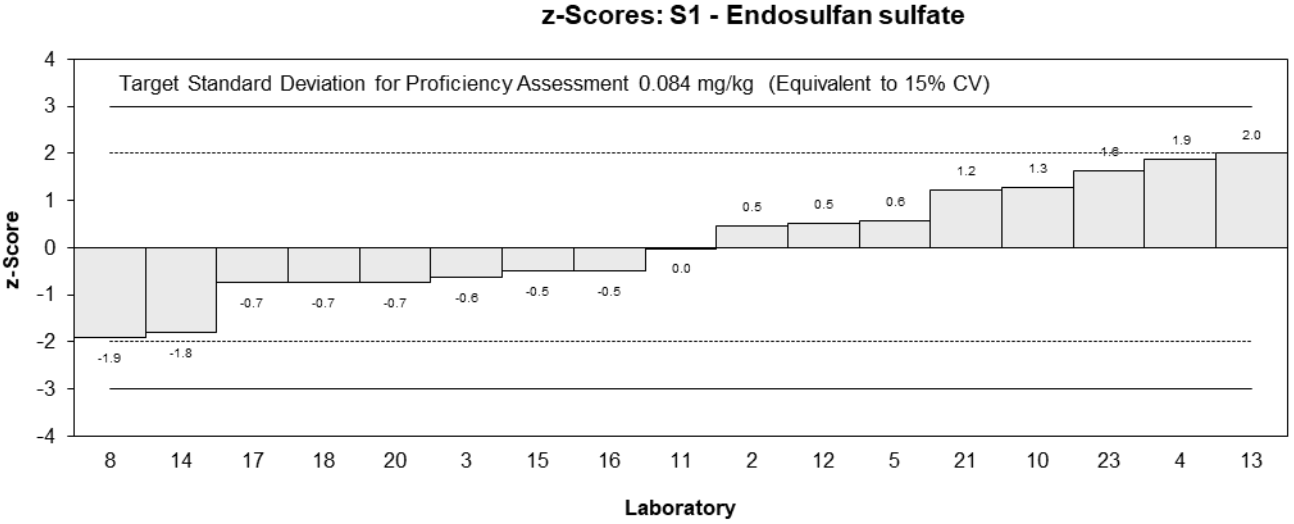
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.010	0.0064	NR		
2	0.6	0.2	80-120	0.45	0.18
3	0.51	0.15	84	-0.62	-0.32
4	0.72	0.22	NR	1.87	0.69
5	0.61	NR	NR	0.57	0.71
8	0.4	0.2	80-120	-1.92	-0.77
9	NT	NT	NT		
10	0.67	0.2	NR	1.28	0.51
11	0.56	0.26	NR	-0.02	-0.01
12	0.606	0.212	94	0.52	0.20
13*	0.87	0.20	101	2.00▼	
14	0.41	0.12	NR	-1.80	-1.10
15	0.52	0.14	NR	-0.50	-0.27
16	0.52	0.21	111	-0.50	-0.19
17	0.5	0.25	NR	-0.74	-0.24
18	0.5	0.2	NR	-0.74	-0.29
19	NR	NR	NR		
20	0.5	NR	NR	-0.74	-0.91
21	0.665	0.1995	NR	1.22	0.49
22	NT	NT	NT		
23	0.7	0.5	NR	1.64	0.27

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.562	0.068
Spike Value	0.753	0.038
Robust Average	0.573	0.071
Max Acceptable Result	0.979	
Median	0.560	0.054
Mean	0.580	
N	17	
Max	0.87	
Min	0.4	
Robust SD	0.12	
Robust CV	21%	


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.562 ± 0.068 mg/kg
Maximum Acceptable Result = 0.979 mg/kg
Results (mg/kg)
Laboratory
8 14 17 18 20 3 15 16 11 2 12 5 21 10 23 4 13 1 9 19 22 Md RA SV


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation for Proficiency Assessment 0.084 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 14 17 18 20 3 15 16 11 2 12 5 21 10 23 4 13
-1.9 -1.8 -0.7 -0.7 -0.7 -0.6 -0.5 -0.5 0.0 0.5 0.5 0.6 1.2 1.3 1.6 1.9 2.0

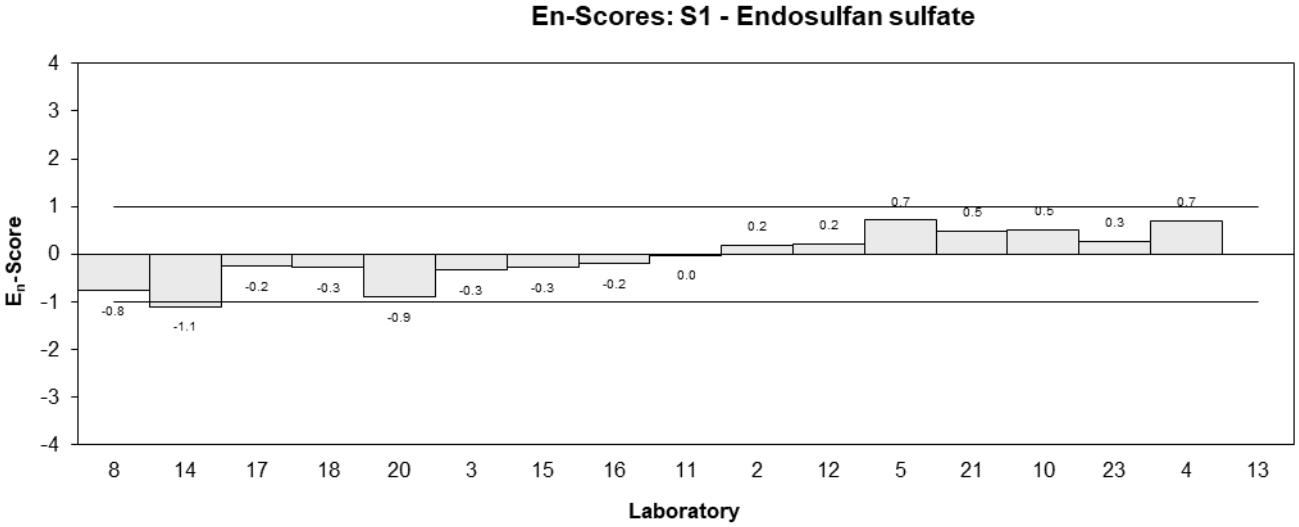

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
8 14 17 18 20 3 15 16 11 2 12 5 21 10 23 4 13
-0.8 -1.1 -0.2 -0.3 -0.9 -0.3 -0.3 -0.2 0.0 0.2 0.2 0.7 0.5 0.5 0.3 0.7

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Glyphosate
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NT	NT	NT
8	1.6	0.5	80-120
9**	0.064	0.022	96
10	<0.02	NR	NR
11	0.939	NR	56
12	NT	NT	NT
13	1.5	0.40	110
14	<0.02	NR	NR
15	NT	NT	NT
16	1.7	0.68	NR
17	NT	NT	NT
18	NT	NT	NT
19	NR	NR	NR
20	NT	NT	NT
21	NT	NT	NT
22	1.86	0.25	104
23	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	1.51	0.08
Robust Average	NA (N<6)	
Median	1.60	0.17
Mean	1.52	
N	5	
Max	1.86	
Min	0.939	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

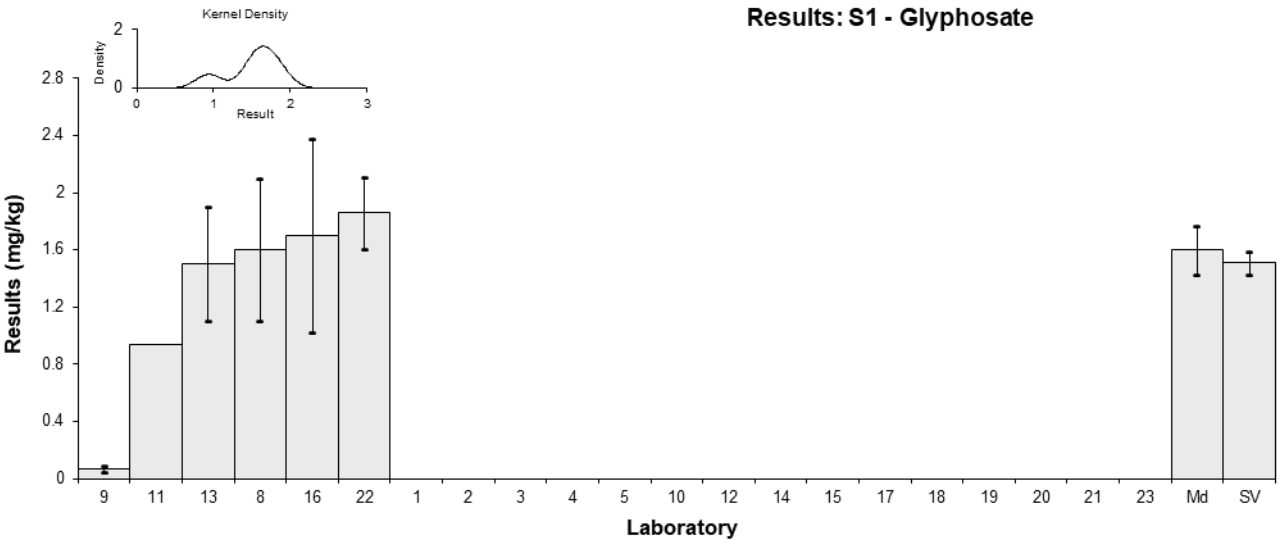

Results: S1 - Glyphosate
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9
11
13
8
16
22
1
2
3
4
5
10
12
14
15
17
18
19
20
21
23
Md
SV

Figure 5

Table 9

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Lindane
Unit	mg/kg

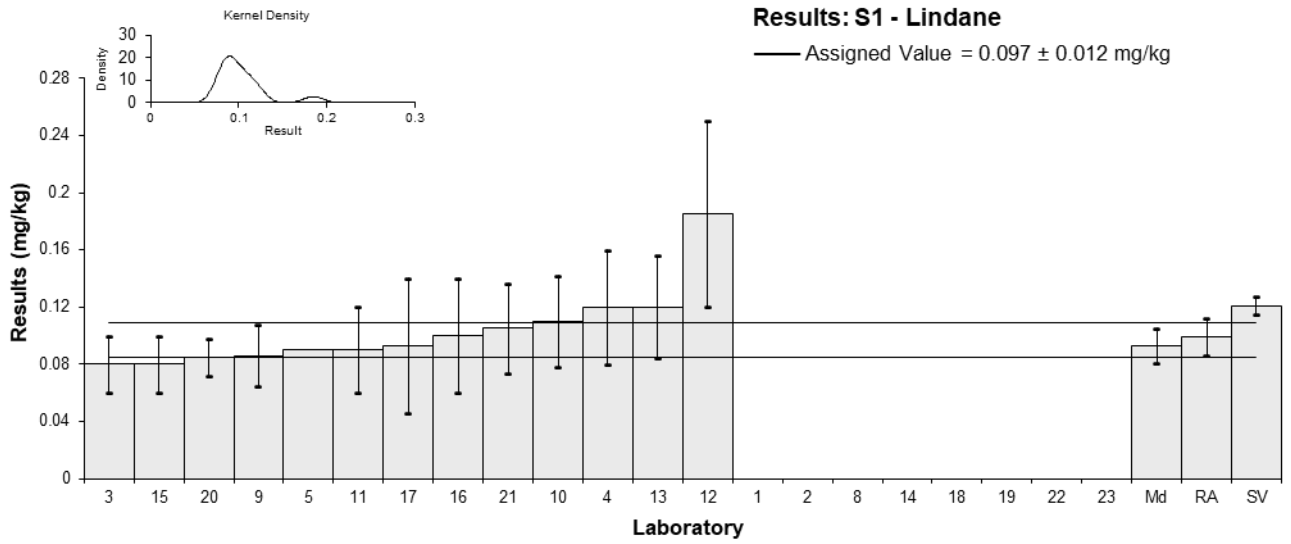
Participant Results

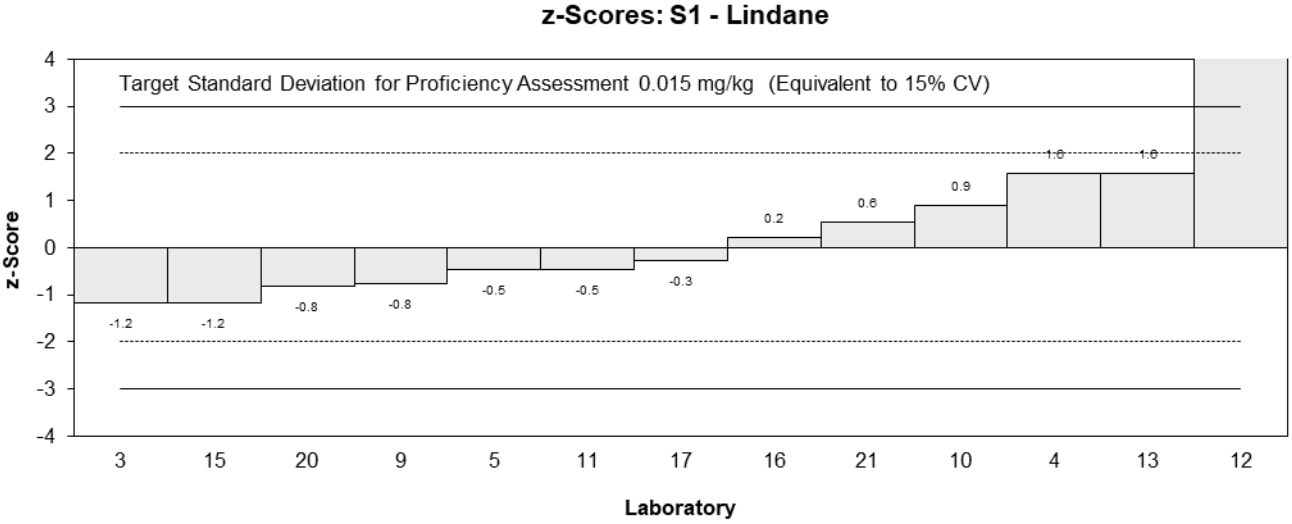
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.010	0.0042	NR		
2	<0.1	NR	80-120		
3	0.08	0.02	84	-1.17	-0.73
4	0.12	0.04	NR	1.58	0.55
5	0.09	NR	NR	-0.48	-0.58
8	<0.1	NR	80-120		
9	0.086	0.0215	117	-0.76	-0.45
10	0.11	0.032	NR	0.89	0.38
11	0.09	0.03	106	-0.48	-0.22
12*	0.185	0.065	96	6.05	1.33
13	0.12	0.036	92	1.58	0.61
14	<0.02	NR	NR		
15	0.08	0.02	NR	-1.17	-0.73
16	0.1	0.04	111	0.21	0.07
17	0.093	0.047	NR	-0.27	-0.08
18	<0.1	NR	NR		
19	NR	NR	NR		
20	0.085	0.013	NR	-0.82	-0.68
21	0.105	0.0315	NR	0.55	0.24
22	NT	NT	NT		
23	<0.5	0.5	NR		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.097	0.012
Spike Value	0.121	0.006
Robust Average	0.099	0.013
Median	0.093	0.012
Mean	0.103	
N	13	
Max	0.185	
Min	0.08	
Robust SD	0.018	
Robust CV	18%	


Kernel Density
Density
Result
Results: S1 - Lindane
Assigned Value = 0.097 ± 0.012 mg/kg
Results (mg/kg)
Laboratory
3 15 20 9 5 11 17 16 21 10 4 13 12 1 2 8 14 18 19 22 23 Md RA SV


z-Scores: S1 - Lindane
Target Standard Deviation for Proficiency Assessment 0.015 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
3 15 20 9 5 11 17 16 21 10 4 13 12

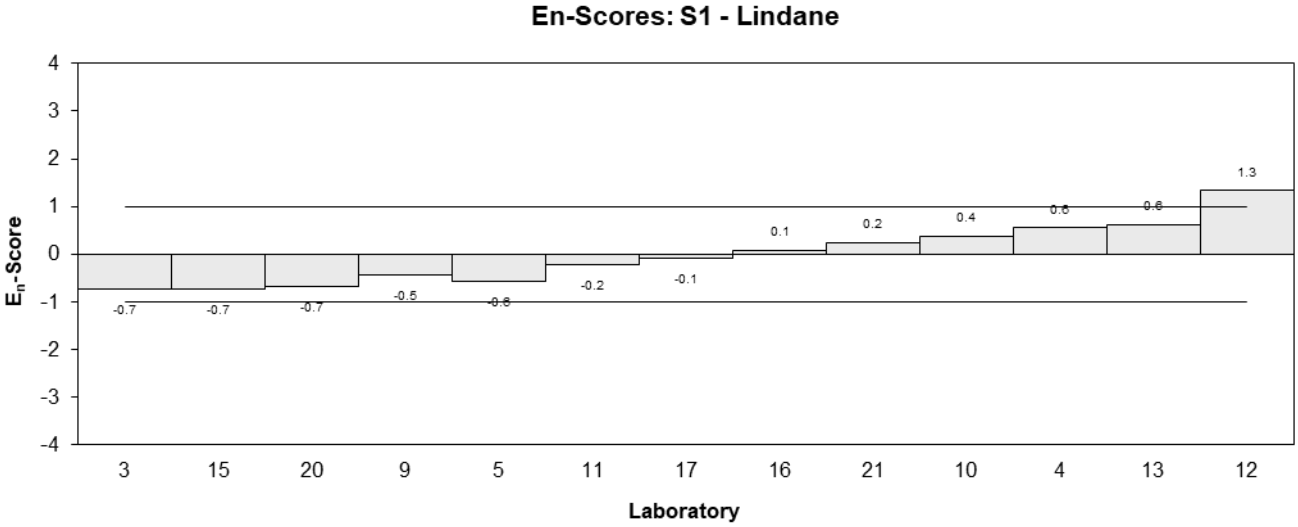

En-Scores: S1 - Lindane
En-Score
Laboratory
3 15 20 9 5 11 17 16 21 10 4 13 12

Figure 6

Table 10

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	MCPA
Unit	mg/kg

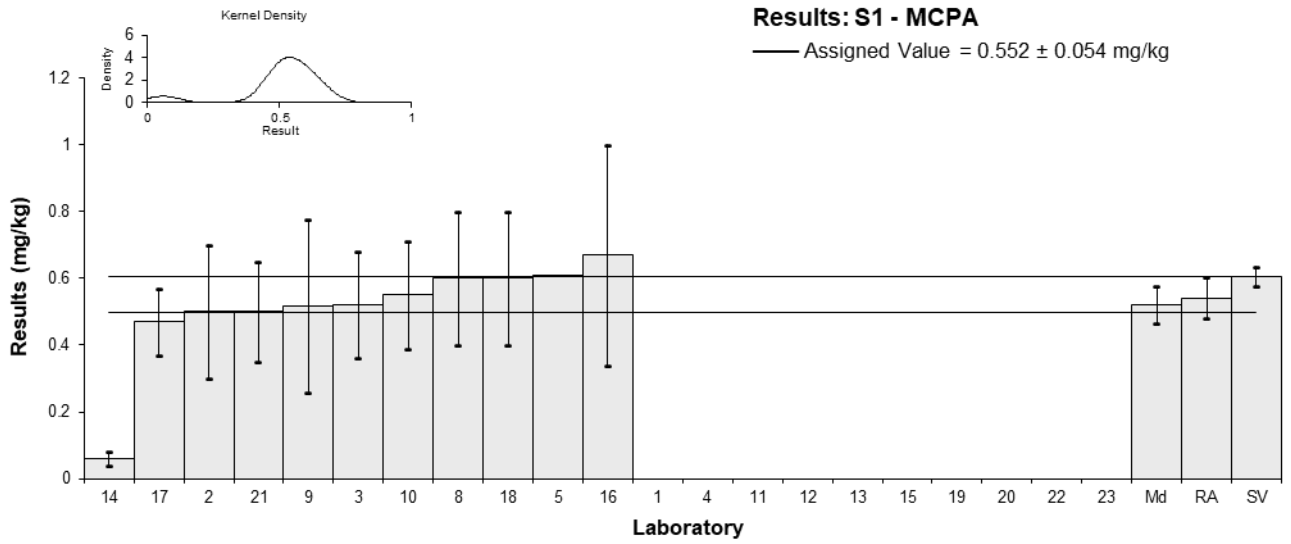
Participant Results

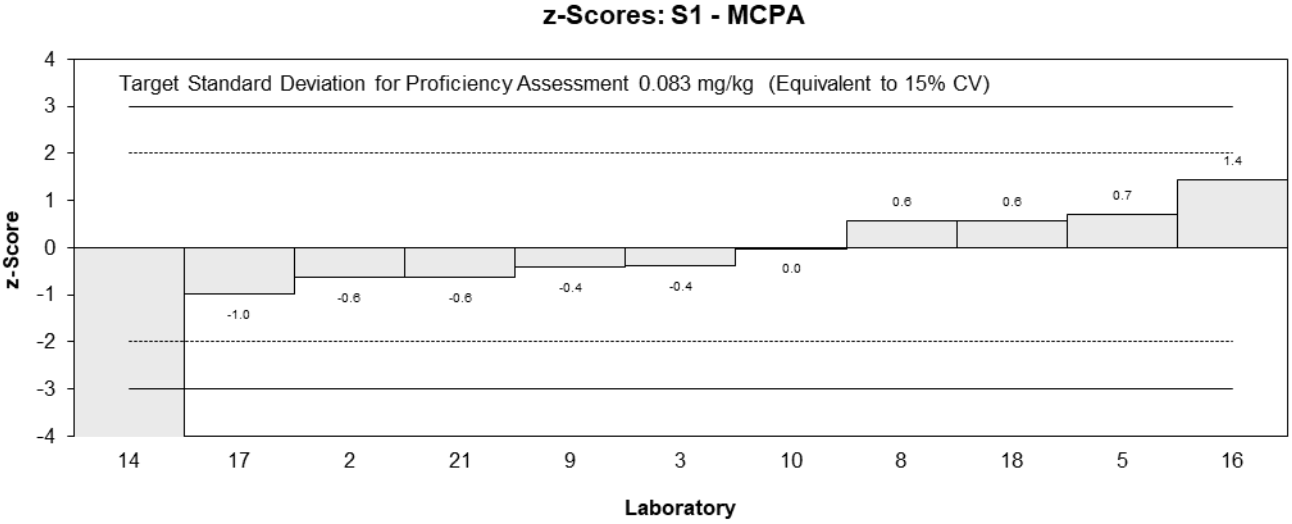
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.010	0.0067	NR		
2	0.5	0.2	80-120	-0.63	-0.25
3	0.52	0.16	87	-0.39	-0.19
4	< 1	NR	NR		
5	0.61	NR	NR	0.70	1.07
8	0.6	0.2	80-120	0.58	0.23
9	0.517	0.258	85	-0.42	-0.13
10	0.55	0.16	NR	-0.02	-0.01
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14*	0.06	0.02	NR	-5.94	-8.54
15	NT	NT	NT		
16	0.67	0.33	NR	1.43	0.35
17	0.47	0.1	NR	-0.99	-0.72
18	0.6	0.2	NR	0.58	0.23
19	NR	NR	NR		
20	NT	NT	NT		
21	0.5	0.15	NR	-0.63	-0.33
22	NT	NT	NT		
23	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.552	0.054
Spike Value	0.606	0.030
Robust Average	0.541	0.061
Median	0.520	0.056
Mean	0.509	
N	11	
Max	0.67	
Min	0.06	
Robust SD	0.080	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - MCPA
Assigned Value = 0.552 ± 0.054 mg/kg
Results (mg/kg)
Laboratory
14 17 2 21 9 3 10 8 18 5 16 1 4 11 12 13 15 19 20 22 23 Md RA SV


z-Scores: S1 - MCPA
Target Standard Deviation for Proficiency Assessment 0.083 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 17 2 21 9 3 10 8 18 5 16
-1.0 -0.6 -0.6 -0.4 -0.4 0.0 0.6 0.6 0.7 1.4

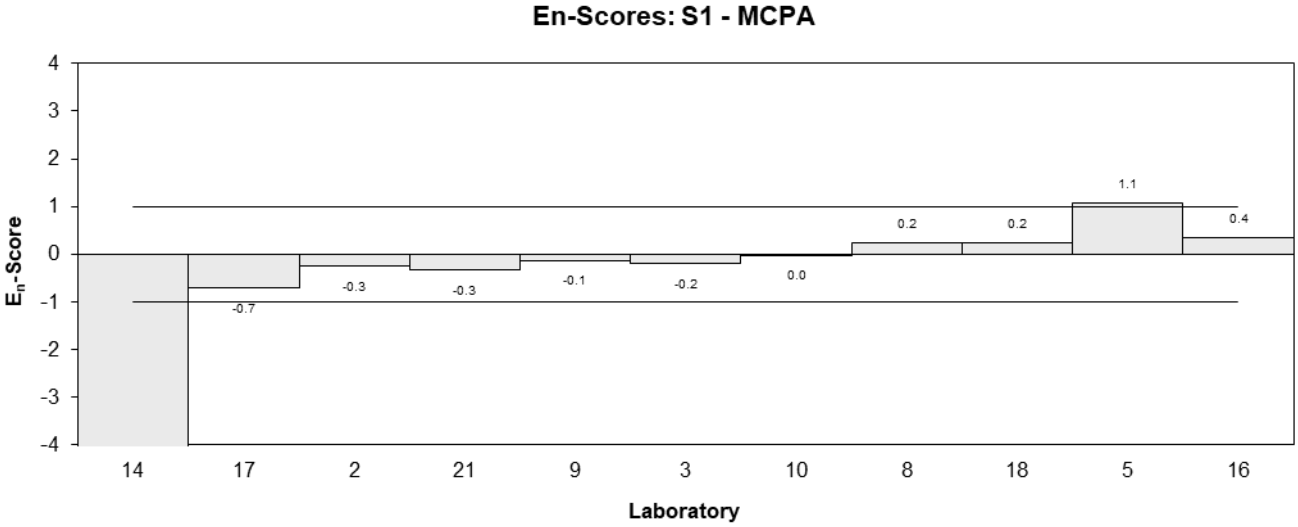

En-Scores: S1 - MCPA
En-Score
Laboratory
14 17 2 21 9 3 10 8 18 5 16
-0.7 -0.3 -0.3 -0.1 -0.2 0.0 0.2 0.2 1.1 0.4

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Atrazine
Unit	mg/kg

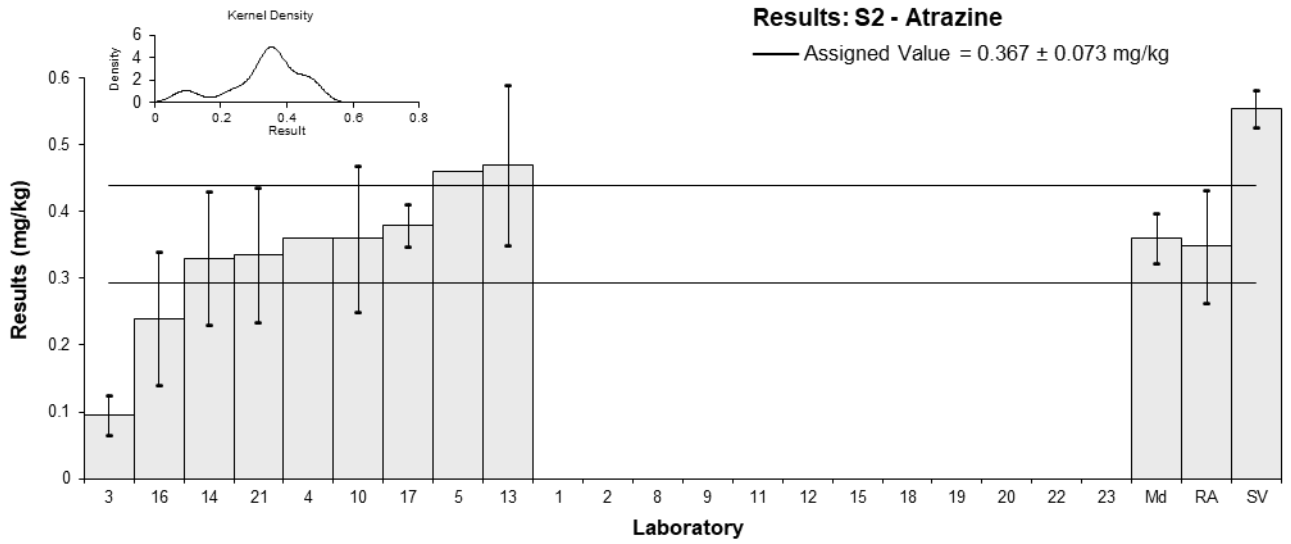
Participant Results

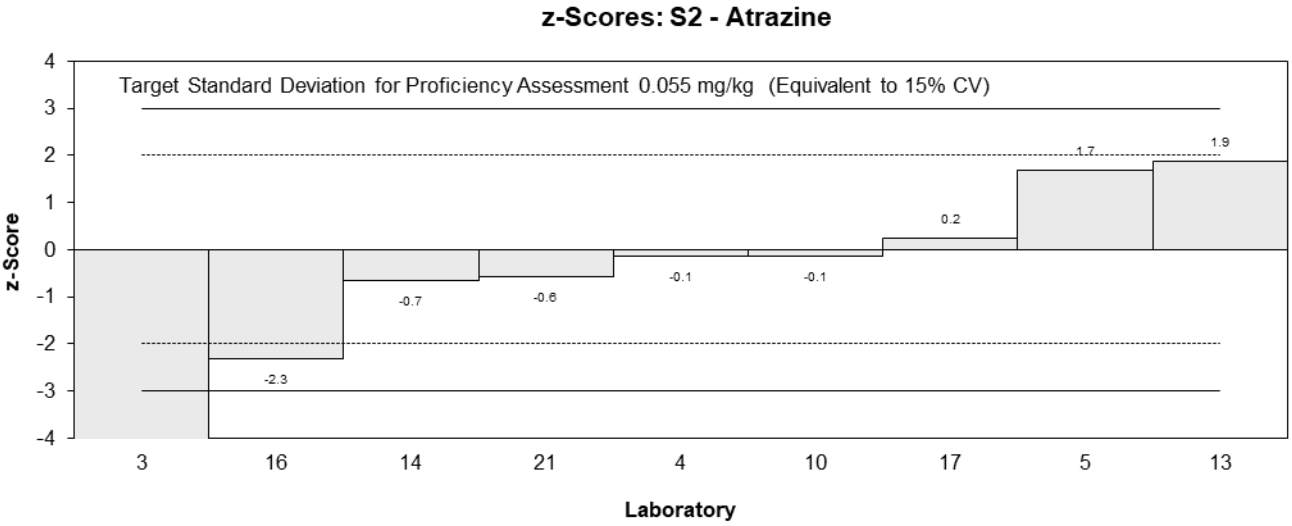
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.006	0.004	NR		
2	<0.5	NR	80-120		
3*	0.095	0.03	96	-4.94	-3.45
4	0.36	NR	NR	-0.13	-0.10
5	0.46	NR	NR	1.69	1.27
8	<0.5	NR	80-120		
9	NT	NT	NT		
10	0.36	0.11	NR	-0.13	-0.05
11	NT	NT	NT		
12	NR	NR	NR		
13	0.47	0.12	97	1.87	0.73
14	0.33	0.10	NR	-0.67	-0.30
15	NT	NT	NT		
16	0.24	0.1	77	-2.31	-1.03
17	0.38	0.032	NR	0.24	0.16
18	<0.5	NR	NR		
19	NR	NR	NR		
20	NT	NT	NT		
21	0.335	0.1005	NR	-0.58	-0.26
22	NT	NT	NT		
23	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.367	0.073
Spike Value	0.555	0.028
Robust Average	0.348	0.084
Median	0.360	0.037
Mean	0.337	
N	9	
Max	0.47	
Min	0.095	
Robust SD	0.10	
Robust CV	29%	


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 0.367 ± 0.073 mg/kg
Results (mg/kg)
Laboratory
3 16 14 21 4 10 17 5 13 1 2 8 9 11 12 15 18 19 20 22 23 Md RA SV


z-Scores: S2 - Atrazine
Target Standard Deviation for Proficiency Assessment 0.055 mg/kg (Equivalent to 15% CV)
z-Score
-2.3
-0.7
-0.6
-0.1
-0.1
0.2
1.7
1.9
Laboratory
3 16 14 21 4 10 17 5 13

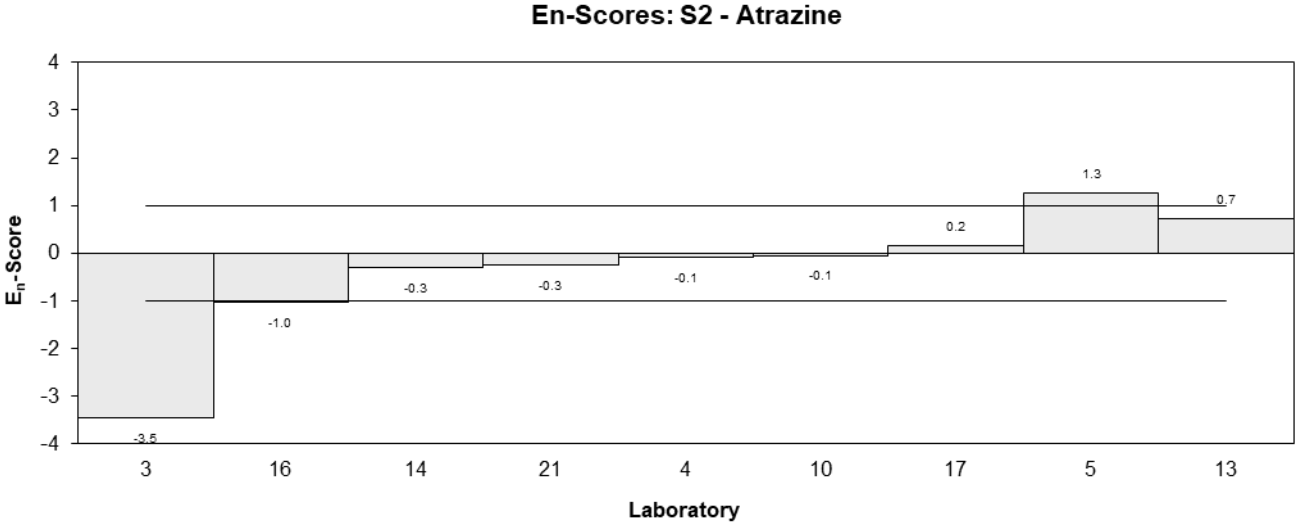

En-Scores: S2 - Atrazine
En-Score
-3.5
-1.0
-0.3
-0.3
-0.1
-0.1
0.2
1.3
0.7
Laboratory
3 16 14 21 4 10 17 5 13

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Diazinon
Unit	mg/kg

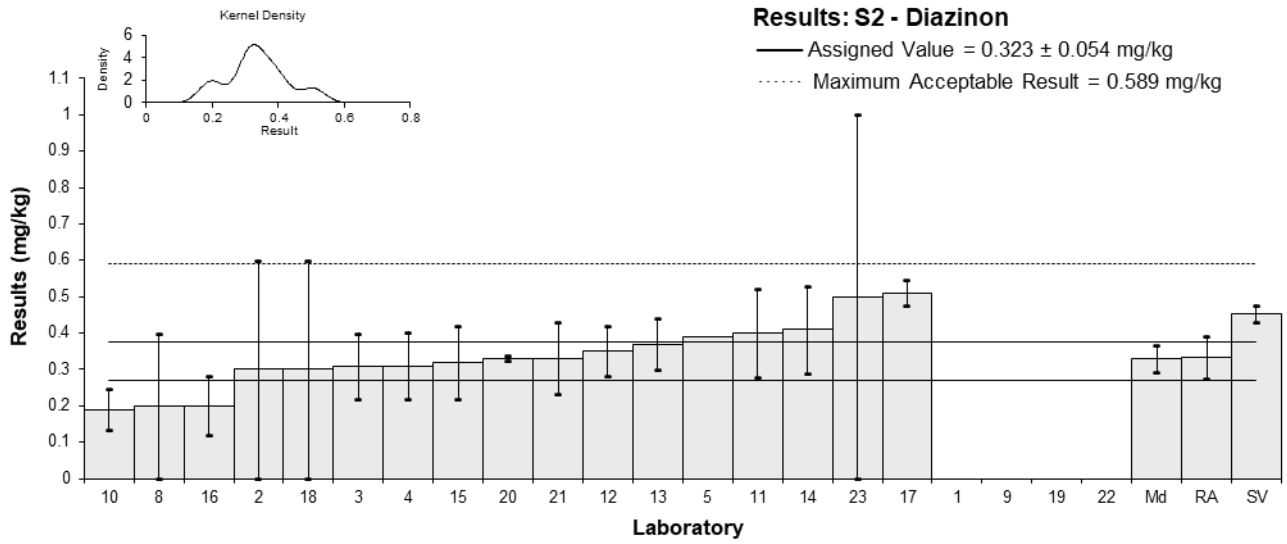
Participant Results

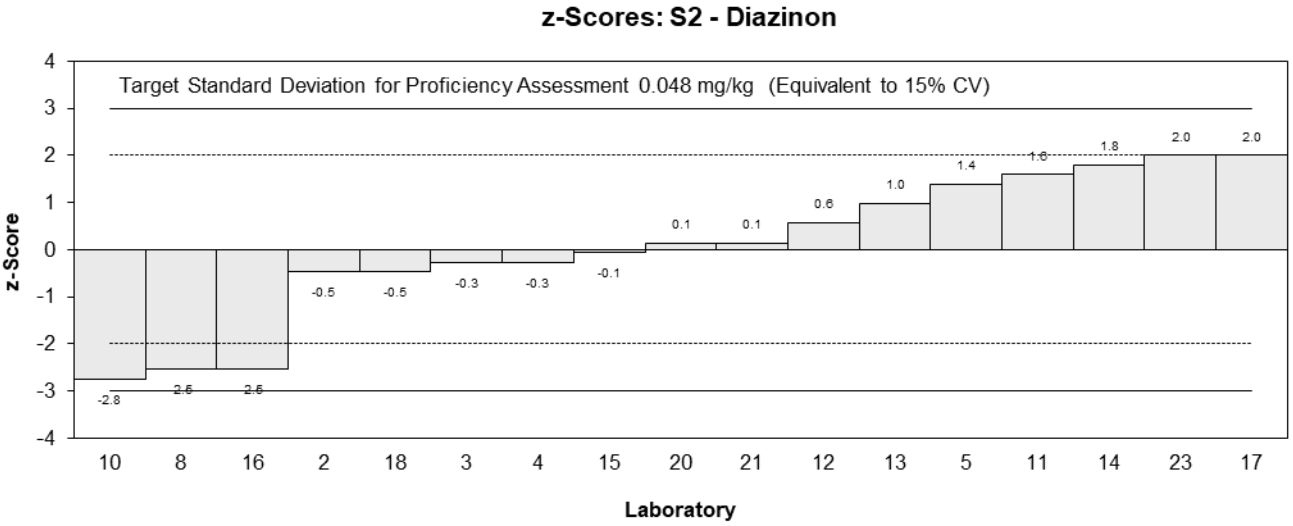
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.003	0.002	NR		
2	0.3	0.3	80-120	-0.47	-0.08
3	0.31	0.09	82	-0.27	-0.12
4	0.31	0.093	NR	-0.27	-0.12
5	0.39	NR	NR	1.38	1.24
8	0.2	0.2	80-120	-2.54	-0.59
9	NT	NT	NT		
10	0.19	0.056	NR	-2.75	-1.71
11	0.400	0.12	104	1.59	0.59
12	0.351	0.070	80	0.58	0.32
13	0.37	0.070	101	0.97	0.53
14	0.41	0.12	NR	1.80	0.66
15	0.32	0.10	NR	-0.06	-0.03
16	0.2	0.081	77	-2.54	-1.26
17*	0.51	0.035	NR	2.00▼	
18	0.3	0.3	NR	-0.47	-0.08
19	NR	NR	NR		
20	0.33	0.007	NR	0.14	0.13
21	0.33	0.099	NR	0.14	0.06
22	NT	NT	NT		
23	0.5	0.5	NR	2.00▼	

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.323	0.054
Spike Value	0.453	0.023
Robust Average	0.333	0.059
Max Acceptable Result	0.589	
Median	0.330	0.036
Mean	0.337	
N	17	
Max	0.51	
Min	0.19	
Robust SD	0.097	
Robust CV	29%	


Kernel Density
Density
Result
Results: S2 - Diazinon
Assigned Value = 0.323 ± 0.054 mg/kg
Maximum Acceptable Result = 0.589 mg/kg
Results (mg/kg)
Laboratory
10 8 16 2 18 3 4 15 20 21 12 13 5 11 14 23 17 1 9 19 22 Md RA SV


z-Scores: S2 - Diazinon
Target Standard Deviation for Proficiency Assessment 0.048 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 8 16 2 18 3 4 15 20 21 12 13 5 11 14 23 17
-2.8 -2.6 -2.6 -0.5 -0.5 -0.3 -0.3 -0.1 0.1 0.1 0.6 1.0 1.4 1.6 1.8 2.0 2.0

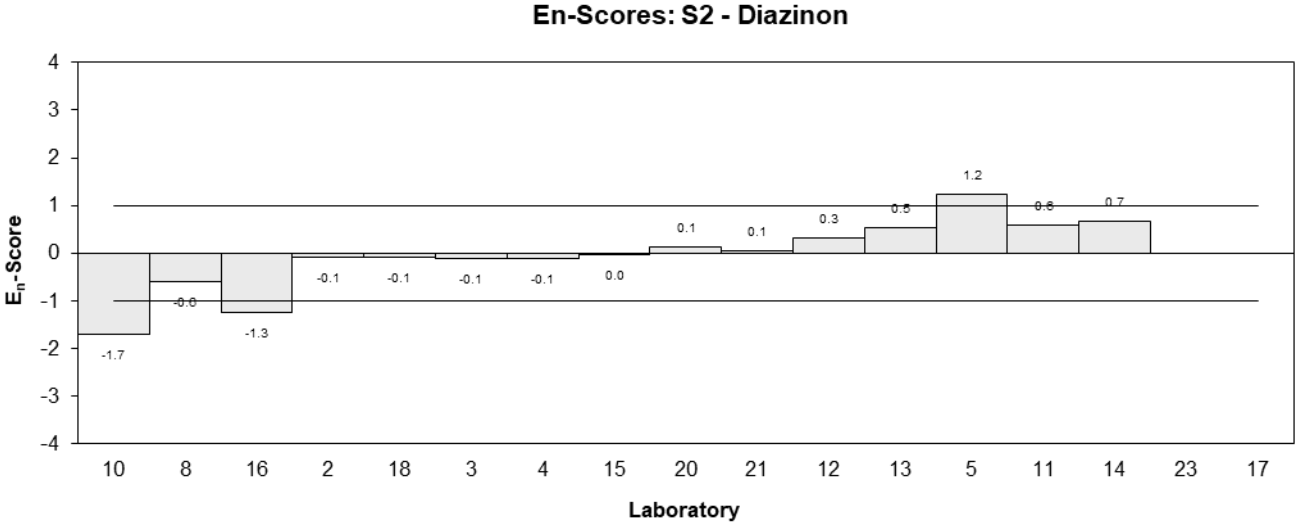

En-Scores: S2 - Diazinon
En-Score
Laboratory
10 8 16 2 18 3 4 15 20 21 12 13 5 11 14 23 17
-1.7 -0.6 -1.3 -0.1 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.3 0.5 1.2 0.6 0.7

Figure 9

Table 13

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Fipronil
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NT	NT	NT
8	0.7	0.3	80-120
9	NT	NT	NT
10	0.58	0.17	NR
11	NT	NT	NT
12	NT	NT	NT
13	0.67	0.14	97
14	0.84	0.25	NR
15	NT	NT	NT
16	<0.5	NR	NR
17	0.61	0.058	NR
18	NT	NT	NT
19	NR	NR	NR
20	NT	NT	NT
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.808	0.040
Robust Average	NA (N<6)	
Median	0.670	0.099
Mean	0.680	
N	5	
Max	0.84	
Min	0.58	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

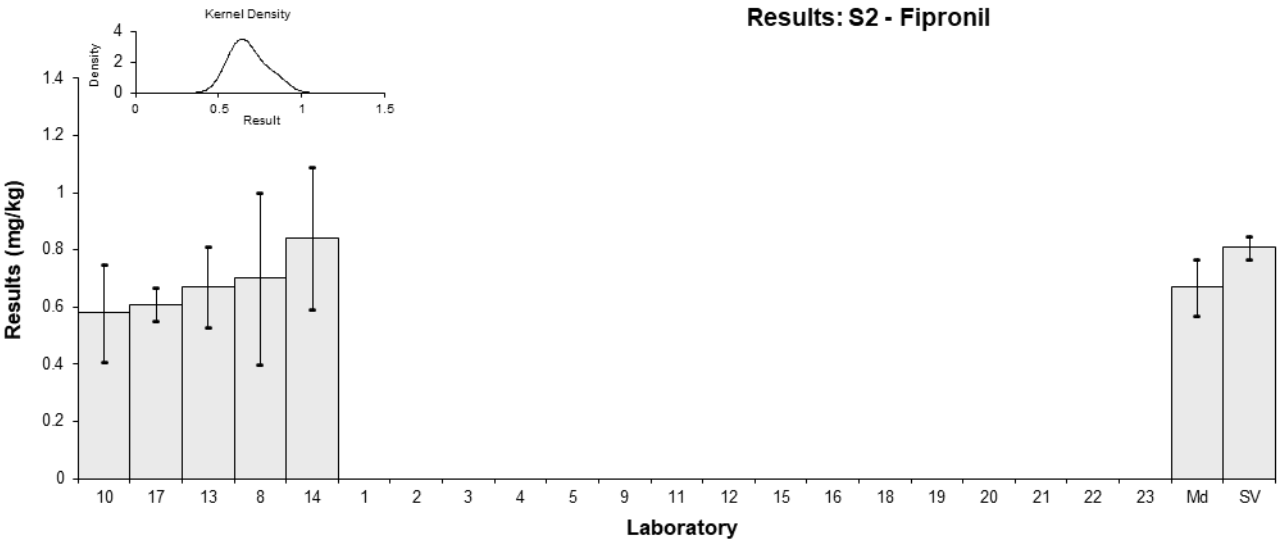

Results: S2 - Fipronil
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
10
17
13
8
14
1
2
3
4
5
9
11
12
15
16
18
19
20
21
22
23
Md
SV

Figure 10

Table 14

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Metsulfuron-methyl
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	< 0.5	NR	NR
5	0.29	NR	NR
8	0.3	0.09	80-120
9	NT	NT	NT
10	0.99	0.3	NR
11	NT	NT	NT
12	NT	NT	NT
13	0.83	0.32	96
14	0.56	0.17	NR
15	NT	NT	NT
16	0.77	0.38	95
17	0.66	0.058	NR
18	NT	NT	NT
19	NR	NR	NR
20	NT	NT	NT
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.759	0.038
Robust Average	0.63	0.28
Median	0.66	0.24
Mean	0.63	
N	7	
Max	0.99	
Min	0.29	
Robust SD	0.30	
Robust CV	48%	

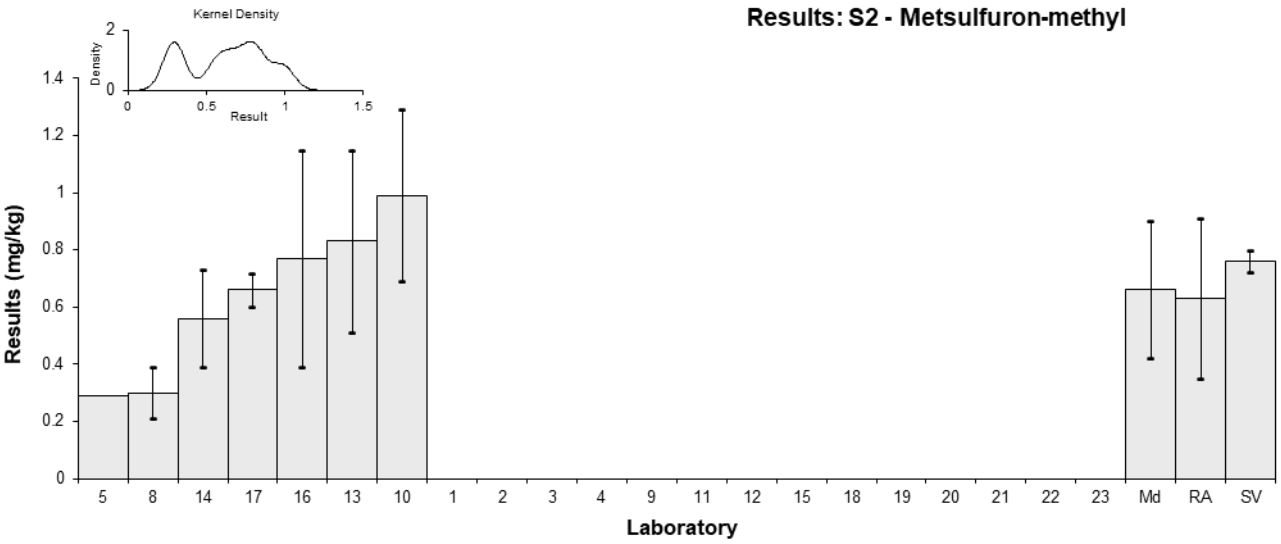

Results: S2 - Metsulfuron-methyl
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5
8
14
17
16
13
10
1
2
3
4
9
11
12
15
18
19
20
21
22
23
Md
RA
SV

Figure 11

Table 15

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Triclopyr
Unit	mg/kg

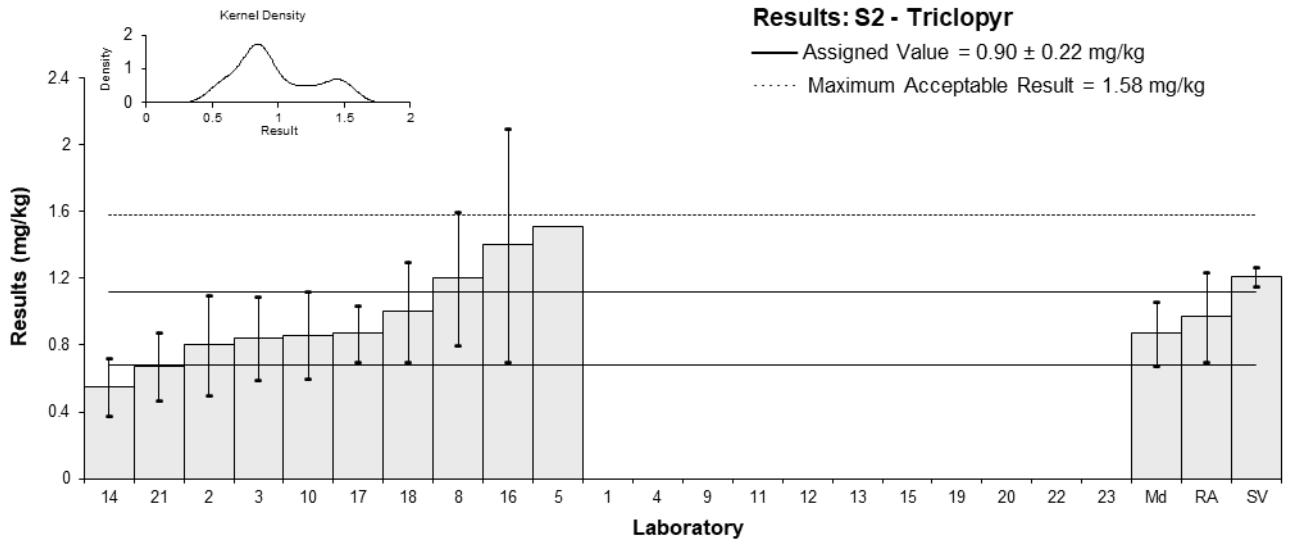
Participant Results

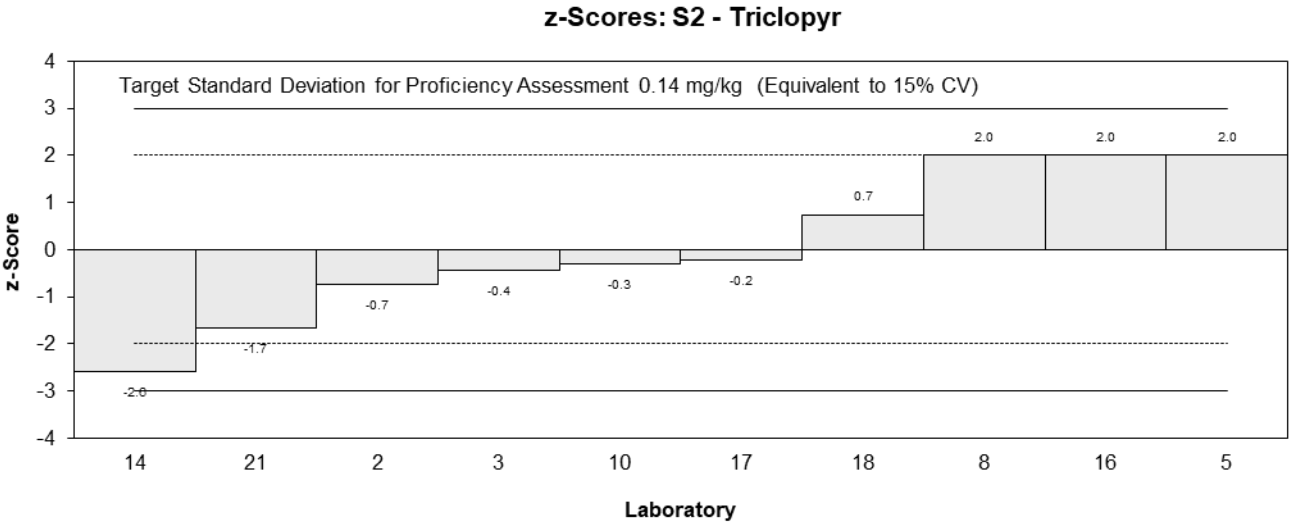
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	<0.010	0.0067	NR		
2	0.8	0.3	80-120	-0.74	-0.27
3	0.84	0.25	84	-0.44	-0.18
4	NT	NT	NT		
5*	1.51	NR	NR	2.00▼	
8	1.2	0.4	80-120	2.00▼	
9	NT	NT	NT		
10	0.86	0.26	NR	-0.30	-0.12
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14	0.55	0.17	NR	-2.59	-1.26
15	NT	NT	NT		
16	1.4	0.7	NR	2.00▼	
17	0.87	0.17	NR	-0.22	-0.11
18	1.0	0.3	NR	0.74	0.27
19	NR	NR	NR		
20	NT	NT	NT		
21	0.675	0.2025	NR	-1.67	-0.75
22	NT	NT	NT		
23	NT	NT	NT		

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.90	0.22
Spike Value	1.21	0.06
Robust Average	0.97	0.27
Max Acceptable Result	1.58	
Median	0.87	0.19
Mean	0.97	
N	10	
Max	1.51	
Min	0.55	
Robust SD	0.35	
Robust CV	36%	


Kernel Density
Density
Result
Results: S2 - Triclopyr
Assigned Value = 0.90 ± 0.22 mg/kg
Maximum Acceptable Result = 1.58 mg/kg
Results (mg/kg)
Laboratory
14 21 2 3 10 17 18 8 16 5 1 4 9 11 12 13 15 19 20 22 23 Md RA SV


z-Scores: S2 - Triclopyr
Target Standard Deviation for Proficiency Assessment 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 21 2 3 10 17 18 8 16 5
-2.6
-1.7
-0.7
-0.4
-0.3
-0.2
0.7
2.0
2.0
2.0

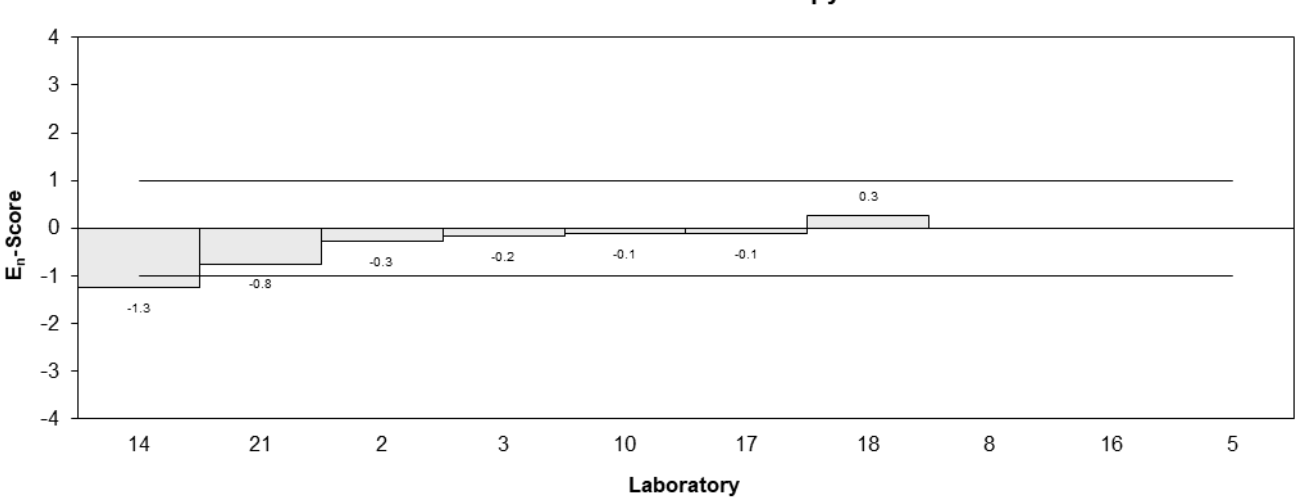

En-Scores: S2 - Triclopyr
En-Score
Laboratory
14 21 2 3 10 17 18 8 16 5
-1.3
-0.8
-0.3
-0.2
-0.1
-0.1
0.3

Figure 12

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. If there were results less than 50% or greater than 150% of the robust average, these were excluded from the calculation of each assigned value.[3,4] The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] Appendix 3 sets out the calculation of the robust average of Sample S2 atrazine and its associated uncertainty.

A proportion of the spiked analyte may be strongly bound to the soil, and so may not be readily extracted and measured. What laboratories measure may best be described as 'extractable analyte', and the result may be influenced by the efficiency of the extraction process used. Therefore, for this study, the assigned value is the best estimate of the amount of 'extractable analyte'.

A comparison of the assigned values and the spiked values is presented in Table 16. The assigned values were within the range of 66% to 91% of the spiked values. Similar ratios have been observed in previous NMIA Pesticides in Soil PT studies,[6] and an assigned value was set if there was a reasonable consensus of results.

Table 16 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Assigned Value / Spiked Value (%)
S1	*p,p'*-DDT	0.227	0.301	75
	Diuron	0.74	1.01	73
	Endosulfan sulfate	0.562	0.753	75
	Glyphosate	1.60*	1.51	106
	Lindane	0.097	0.121	80
	MCPA	0.552	0.606	91
S2	Atrazine	0.367	0.555	66
	Diazinon	0.323	0.453	71
	Fipronil	0.670*	0.808	83
	Metsulfuron-methyl	0.63†	0.759	83
	Triclopyr	0.90	1.21	74

*Median (assigned value not set).
†Robust Average (assigned value not set).

No assigned values were set for Sample S1 glyphosate and Sample S2 fipronil as there were too few numeric results reported for these analytes, however most reported numeric results were in good consensus with each other as well as the spiked value. No assigned value was set for Sample S2 metsulfuron-methyl as the reported numeric results were too varied. For these analytes, participants may still compare their results with the descriptive statistics and spiked values as presented in Section 5.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, the metrological traceability of the assigned values has not been established.

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded uncertainty associated with their results and the basis of this uncertainty evaluation. It is a requirement of ISO/IEC 17025 that laboratories have procedures to evaluate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.[9]

Of 122 numeric results, 109 (89%) were reported with an associated expanded MU. Participants used a wide variety of procedures to evaluate their uncertainties (Table 3). The magnitude of the reported expanded uncertainties was within the range 2.1% to 100% of the reported value. In general, an expanded uncertainty of less than 15% is likely to be unrealistically small for the routine measurement of a pesticide residue, while over 50% is likely to be too large to be fit-for-purpose. In this study, 92 (84%) expanded uncertainties were between 15% and 50% relative; eight expanded uncertainties were less than 15% relative and nine were greater than 50% relative.

Laboratory **5** reported being accredited to ISO/IEC 17025, however none of their reported results had an associated uncertainty.

Laboratories **4**, **8**, and **20** reported uncertainties for all except one of their results each; these participants all reported being accredited to ISO/IEC 17025. Laboratory **11** also reported uncertainties for all except one of their results, however they did not report their accreditation status.

Laboratories **2**, **8**, **18** and **23** reported a relative expanded uncertainty of 100% for at least one of their reported numeric results.

Participants were also requested to report the coverage factor associated with their uncertainties (Table 3). All participants reporting their coverage factor (13) reported k = 2.

Uncertainties associated with results returning an acceptable *z*-score but an unacceptable E_n-score may have been underestimated.

Laboratories **1** and **23** attached evaluations of expanded MU for results reported as less than their limit of reporting (LOR). An evaluation of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

In some cases, results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write the uncertainty to no more than two significant figures, and then to write the result with the corresponding number of decimal places. For example, instead of 0.335 ± 0.1005 mg/kg, report 0.34 ± 0.10 mg/kg.[10]

6.3 z-Score

Target SDs for proficiency assessment equivalent to 15% PCV were used to calculate *z*-scores for all scored analytes. CVs predicted by the Thompson-Horwitz equation,[8] between-laboratory CVs and target SDs for proficiency assessment (as PCVs) for this study are presented for comparison in Table 17.

Table 17 Comparison of Thompson-Horwitz CVs, Between-Laboratory CVs and Target SDs

Sample	Analyte	Assigned Value (mg/kg)	Thompson-Horwitz CV‡ (%)	Between-Laboratory CV§ (%)	Target SD (as PCV) (%)
S1	*p,p*'-DDT	0.227	20	28	15
	Diuron	0.74	17	33	15
	Endosulfan sulfate	0.562	17	19	15
	Glyphosate	1.60*	15	26	Not Set
	Lindane	0.097	22	17	15
	MCPA	0.552	17	12	15
S2	Atrazine	0.367	19	23	15
	Diazinon	0.323	19	27	15
	Fipronil	0.670*	17	17	Not Set
	Metsulfuron-methyl	0.63†	17	48	Not Set
	Triclopyr	0.90	16	30	15

*Median (assigned value not set).
†Robust Average (assigned value not set).
‡Calculated from the assigned value.
§Robust between-laboratory CV (outliers removed where applicable).

To account for possible low bias in consensus values due to participants using inefficient extraction or analytical techniques, a total of eight *z*-scores were adjusted across the following analytes: Sample S1 *p,p*'-DDT and endosulfan sulfate, and Sample S2 diazinon and triclopyr. A maximum acceptable result was set as the spiked value plus two target SDs of the spiked value. Results lower than the maximum acceptable result but with a *z*-score greater than 2.0 had their *z*-score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. *z*-Scores for results higher than the maximum acceptable result and *z*-scores less than 2.0 were left unaltered.

Of 104 results for which *z*-scores were calculated, 90 (87%) returned a *z*-score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **3**, **5**, **10**, **16**, **17** and **21** reported results for all eight analytes for which *z*-scores were calculated. Of these participants, Laboratories **5**, **17** and **21** returned acceptable *z*-scores for all eight scored analytes.

Seven participants received acceptable *z*-scores for all analytes they reported results for: **13** (6), **2** (5), **4** (5), **18** (5), **9** (4), **11** (4) and **23** (2).

Laboratories **1**, **19** and **22** did not report numeric results for any scored analyte in this study.

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 13 and by analyte in Figure 14.

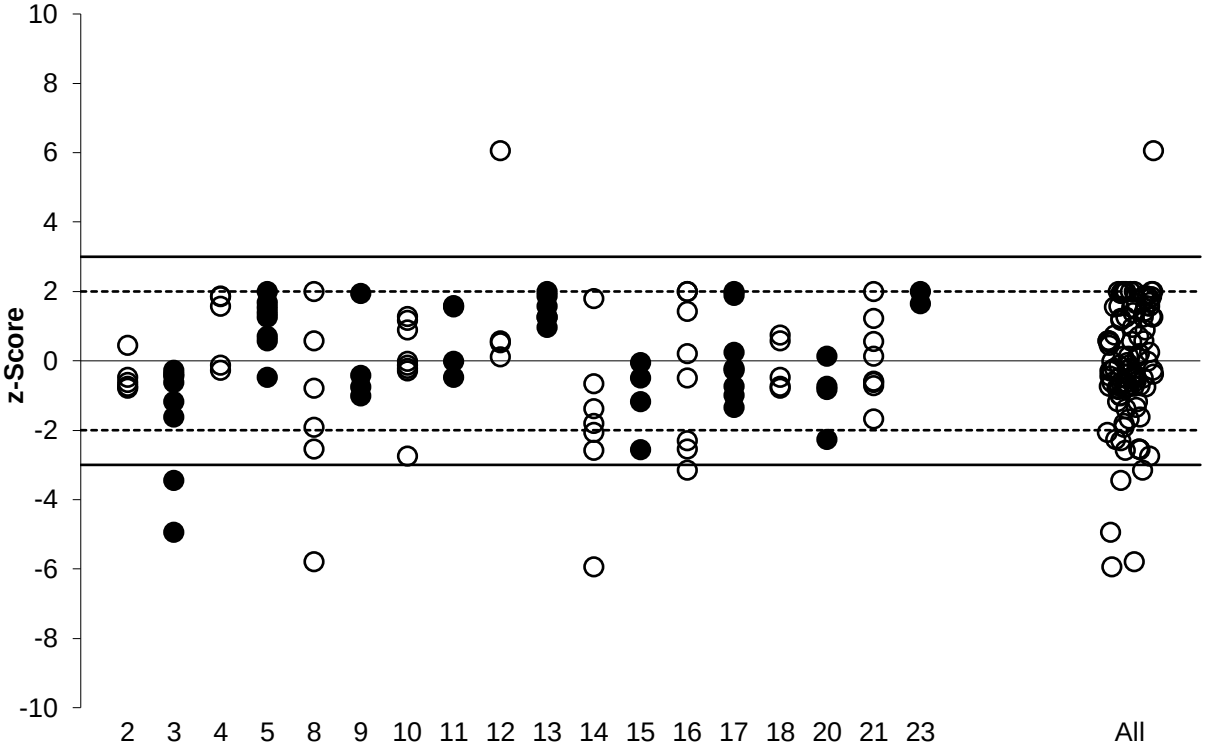


Figure 13 *z*-Score Dispersal by Laboratory

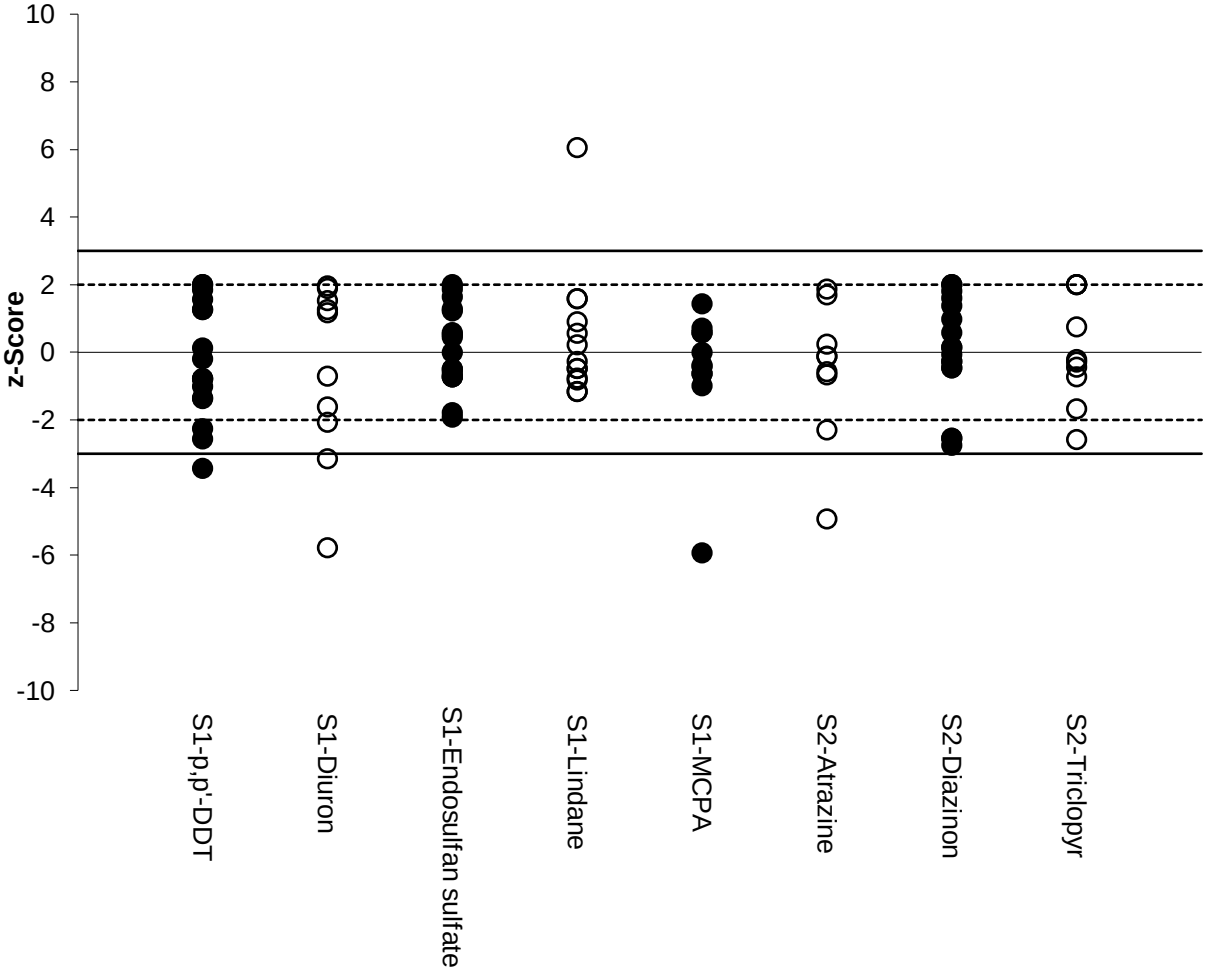


Figure 14 *z*-Score Dispersal by Analyte

6.4 E_n-Score

Where a laboratory did not report an uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score. For results whose *z*-scores were adjusted as discussed in Section 6.3, no E_n-score has been reported.

Of 96 results for which E_n-scores were calculated, 78 (81%) were acceptable with $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Five participants received acceptable E_n-scores for all analytes they reported results for: **2** (5), **4** (5), **18** (5), **9** (4) and **11** (4).

Some participants had results where the *z*-score was adjusted as described above, and so E_n-scores were only calculated for some of their results. Of these participants, three participants received acceptable E_n-scores for all scored analytes that they reported results for: **21** (7), **13** (5) and **23** (1).

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 15.

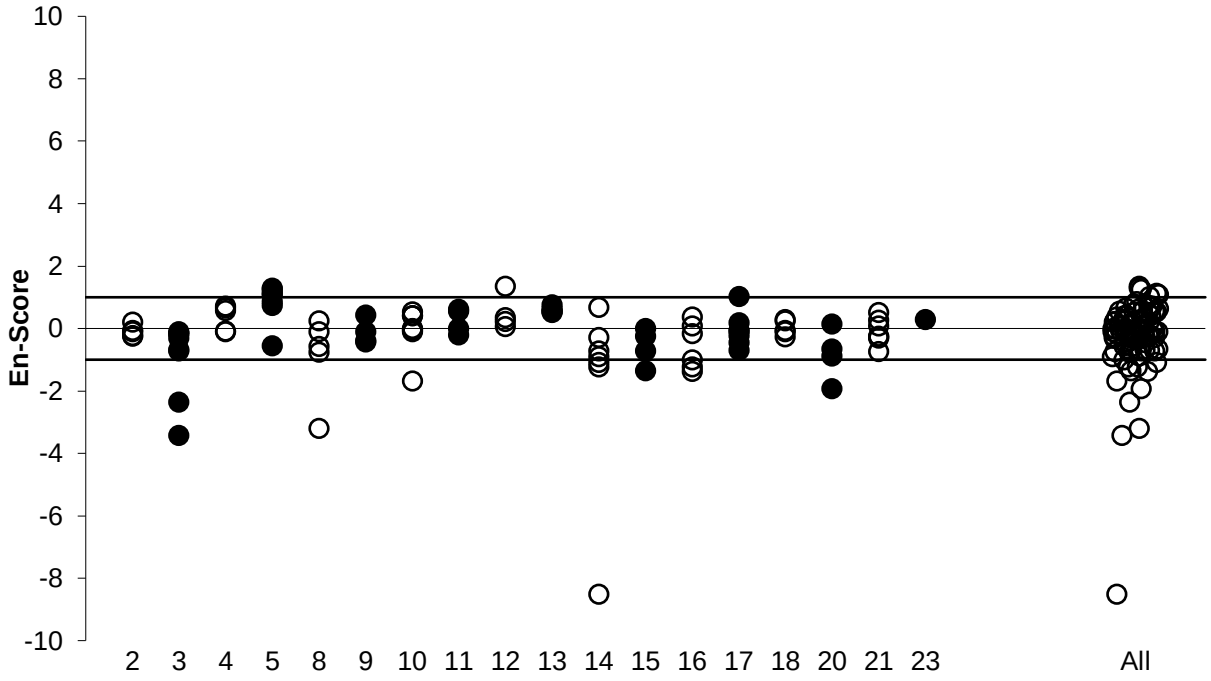


Figure 15 E_n-Score Dispersal by Laboratory

6.5 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential analytes that could have been spiked into the test samples (Table 2). Of these analytes, eleven were spiked into the samples for this study. Participants were not required to test for all potential analytes, and were requested to report 'NT' (for 'Not Tested') for pesticides they did not analyse the samples for.

A summary of the participants' testing of the spiked pesticides is presented in Table 18.

Laboratories **8**, **10**, **14**, **16** and **19** reported testing for all spiked pesticides in this study. Other than these participants, the proportion of pesticides analysed by each participant ranged from 9% to 91%.

No pesticide was analysed by all participants. The proportion of participants analysing each pesticide in this study ranged from 33% (fipronil) to 95% (p,p'-DDT and lindane).

Table 18 Summary of Pesticides Analysed by Participants

Lab. Code	Atrazine	p,p'-DDT	Diazinon	Diuron	Endosulfan sulfate	Fipronil	Glyphosate	Lindane	MCPA	Metsulfuron-methyl	Triclopyr	Proportion of Analytes (%)
1	✓	✓	✓	✓	✓	NT	NT	✓	✓	NT	✓	73
2	✓	✓	✓	NT	✓	NT	NT	✓	✓	NT	✓	64
3	✓	✓	✓	✓	✓	NT	NT	✓	✓	NT	✓	73
4	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	NT	73
5	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	82
8	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
9	NT	✓	NT	✓	NT	NT	✓	✓	✓	NT	NT	45
10	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
11	NT	✓	✓	NT	✓	NT	✓	✓	NT	NT	NT	45
12	✓	✓	✓	NT	✓	NT	NT	✓	NT	NT	NT	45
13	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	NT	82
14	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
15	NT	✓	✓	NT	✓	NT	NT	✓	NT	NT	NT	36
16	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
17	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	91
18	✓	✓	✓	NT	✓	NT	NT	✓	✓	NT	✓	64
19	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
20	NT	✓	✓	NT	✓	NT	NT	✓	NT	NT	NT	36
21	✓	✓	✓	✓	✓	NT	NT	✓	✓	NT	✓	73
22	NT	NT	NT	NT	NT	NT	✓	NT	NT	NT	NT	9
23	NT	✓	✓	NT	✓	NT	NT	✓	NT	NT	NT	36
Proportion of Participants (%)	71	95	90	62	90	33	43	95	67	43	57	

6.6 False Negatives

Six participants reported false negative results (Table 19). These are analytes present in the samples which a participant tested for but did not report a numeric result; for example, participants reporting a 'less than' result (< *x*) when the assigned value was higher than their limit of reporting (LOR), or participants that did not report anything. For analytes where no assigned value was set, results have only been considered to be false negatives where the consensus value and spiked value were significantly higher than the participants' LOR (i.e. the consensus value minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 19 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Result[§] (mg/kg)
1[‡]	S1	*p,p*'-DDT	0.227	0.301	<0.010
		Diuron	0.74	1.01	<0.006
		Endosulfan sulfate	0.562	0.753	<0.010
		Lindane	0.097	0.121	<0.010
		MCPA	0.552	0.606	<0.010
	S2	Atrazine	0.367	0.555	<0.006
		Diazinon	0.323	0.453	<0.003
		Triclopyr	0.9	1.21	<0.010
10	S1	Glyphosate	1.60*****	1.51	<0.02
12	S2	Atrazine	0.367	0.555	NR
14	S1	Glyphosate	1.60*****	1.51	<0.02
		Lindane	0.097	0.121	<0.02
16	S2	Fipronil	0.670*****	0.808	<0.5
19	S1	*p,p*'-DDT	0.227	0.301	NR
		Diuron	0.74	1.01	NR
		Endosulfan sulfate	0.562	0.753	NR
		Glyphosate	1.60*****	1.51	NR
		Lindane	0.097	0.121	NR
		MCPA	0.552	0.606	NR
	S2	Atrazine	0.367	0.555	NR
		Diazinon	0.323	0.453	NR
		Fipronil	0.670*****	0.808	NR
		Metsulfuron-methyl	0.63[†]	0.759	NR
		Triclopyr	0.9	1.21	NR

*Median (assigned value not set).
[†]Robust Average (assigned value not set).
[‡]After the release of the Interim Report, Laboratory **1** reported that they had submitted Sample S2 results as Sample S1, and vice versa. If results were switched between the two samples, this participant would not have had any false negative results.
[§]Results reported as NR may or may not be false negatives, depending on the participant's actual LOR.

6.7 Reporting of Additional Analytes

Eleven participants reported additional analytes that were not spiked into the test samples by the study coordinator (Table 20).

Several participants reported results for *p,p*'-DDD and/or *p,p*'-DDE in Sample S1, however this sample was spiked with *p,p*'-DDT only. Samples were stored at 4 ^{o}C and so there was unlikely to be significant breakdown of *p,p*'-DDT. The *p,p*'-DDD and *p,p*'-DDE reported by participants may be the result of the breakdown of *p,p*'-DDT during analysis in, for example, hot GC injection ports.[11] Participants reporting these breakdown products at significant levels should revise their method to minimise the breakdown.

In general, participants should take care to avoid any cross-contamination between samples.

Table 20 Non-Spiked Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
1*	S1	Atrazine	0.276	0.045	NR
		Diazinon	0.271	0.058	NR
		Triclopyr	0.91	0.17	NR
	S2	*p,p*'-DDD	0.0127	0.0066	NR
		p,p'-DDT	0.148	0.086	NR
		Total DDT	0.16	0.087	NR
		Diuron	0.46	0.12	NR
		Endosulfan sulfate	0.4	0.25	NR
		Lindane	0.061	0.018	NR
		MCPA	0.549	0.045	NR
3	S1	*p,p*'-DDD	0.048	0.01	84
5	S1	*p,p*'-DDD	0.06	NR	NR
8	S2	*p,p*'-DDT	0.2	NR	NR
		Total DDT	0.2	NR	NR
		Diuron	0.097	0.03	NR
		Endosulfan sulfate	0.4	NR	NR
9	S1	*p,p*'-DDD	0.0242	0.00968	130
10	S1	*p,p*'-DDD	0.031	0.0092	NR
14	S1	2,4-D	0.04	0.01	NR
		p,p'-DDD	0.02	0.01	NR
	S2	2,4-D	0.04	0.01	NR
15	S1	*p,p*'-DDD	0.05	0.01	NR
17	S1	*p,p*'-DDD	0.011	0.006	NR
20	S1	*p,p*'-DDE	0.02	0.011	NR
		Heptachlor epoxide	0.03	0.02	NR
		beta-BHC	0.093	0.01	NR
	S2	Parathion	0.01	0.0012	NR

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
22	S2	Glyphosate	0.31	0.13	104

*After the release of the Interim Report, Laboratory **1** reported that they had submitted Sample S2 results as Sample S1, and vice versa. If results were switched between the two samples, this participant would not have reported additional analytes not spiked into the test samples (except for *p,p*'-DDD).

Sample S1 was spiked with *p,p*'-DDT, and this was the scored analyte. Several participants also reported a total DDT value for this sample, which was not scored for this study. These results are presented in Table 21 for information only.

Table 21 Reported Results for Sample S1 Total DDT

Lab. Code	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
2	0.2	0.2	NR
3	0.11	0.03	86
4	0.29	0.09	NR
5	0.33	NR	NR
8	0.2	0.2	NR
9	0.1925	0.968	NR
10	0.24	0.073	NR
11	0.280	0.09	106
12	0.231	NR	NR
13	0.28	0.060	94
15	0.19	0.05	NR
16	0.31	0.12	111
17	0.189	NR	NR
18	0.2	0.2	NR
20	0.17	0.01	NR
21	0.31	0.093	NR

6.8 Participants' Analytical Methods

Results that were removed from all statistical calculations in Section 5 have also been removed from all discussion in this section.

A variety of analytical methods were used for the different analytes (Appendix 4).

For scored analytes, participants reported using a sample size between 0.1 g and 50 g (entire sample) per analysis. The most common sample size used for analysis was 10 g. There was no significant trend between the results obtained and the sample mass used for analysis (Figure 16).

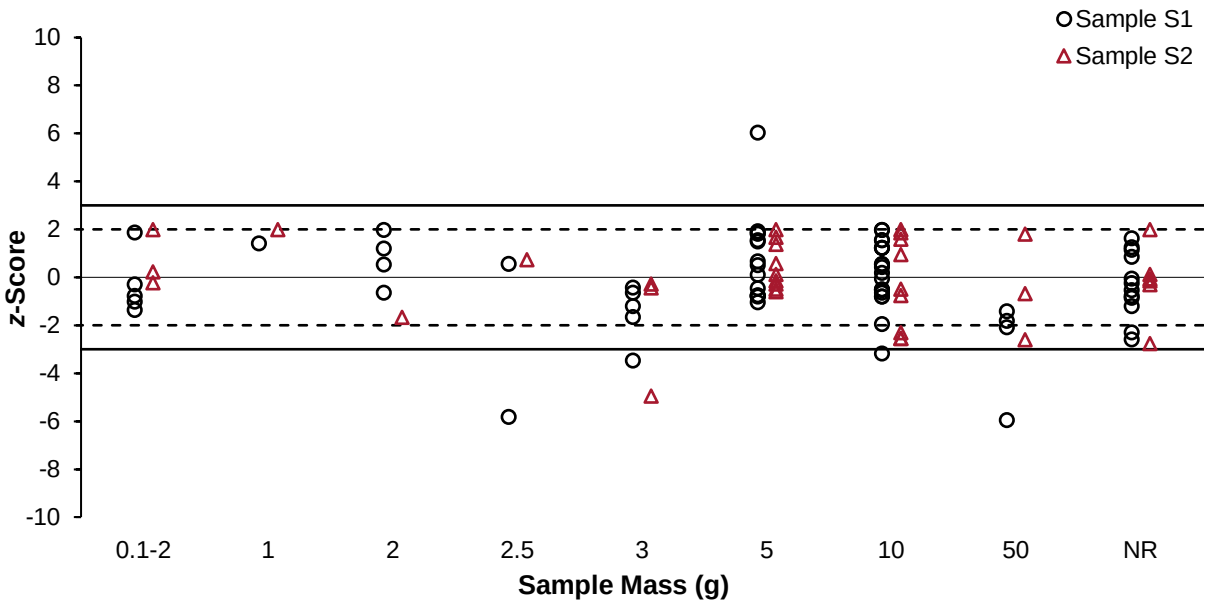


Figure 16 *z*-Score vs Sample Mass Used for Analysis

Participants used a variety of extraction techniques including solid-liquid extraction (SLE), QuEChERS and sonication. Participants also used a range of extraction solvents, including acetone (ACE), acetonitrile (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), hexane (HEX), methanol (MeOH), toluene (TOL), water, and combinations of these solvents. Several participants reported using a clean-up step for their analyses.

Instrumental techniques employed by participants for the analysis of pesticides of interest in this study included gas chromatography (GC) coupled with mass spectrometry (MS), tandem mass spectrometry (MS/MS), electron capture detection (ECD), or flame photometric detection (FPD), liquid chromatography (LC) coupled with MS, MS/MS, and high performance liquid chromatography (HPLC) coupled with diode array detection (DAD).

Plots of results reported and methodology used are presented in Figures 17 to 27. Methodologies are listed in order of reported extraction technique, extraction solvent(s), clean-up (if applicable) and instrument. If a participant did not report any methodology, this has been recorded as 'NR' (for 'Not Reported'). Where charts refer to n = *x*, this corresponds to *x* number of participants using that methodology. For scored analytes, participants' results yielding unacceptable *z*-scores ($|z| \geq 3.0$) have been circled for reference.

There was a very wide variety of methodologies employed across the analytes in this study, and no significant trend was observed for most analytes. There may be a relationship between participants using SLE and diuron low recovery.

Endosulfan sulfate, lindane and MCPA did not present a problem to laboratories' analytical techniques, with excellent agreement between reported results across a wide range of methodologies.

Glyphosate and fipronil were analysed by a limited number of laboratories, however reported results were generally in good agreement with each other as well as the spiked value for these analytes.

For metsulfuron-methyl, there was no consistency between different methodologies used by participants. Participants reporting results biased low relative to the spiked value may need to review, for example, the extraction efficiency of their methodology.

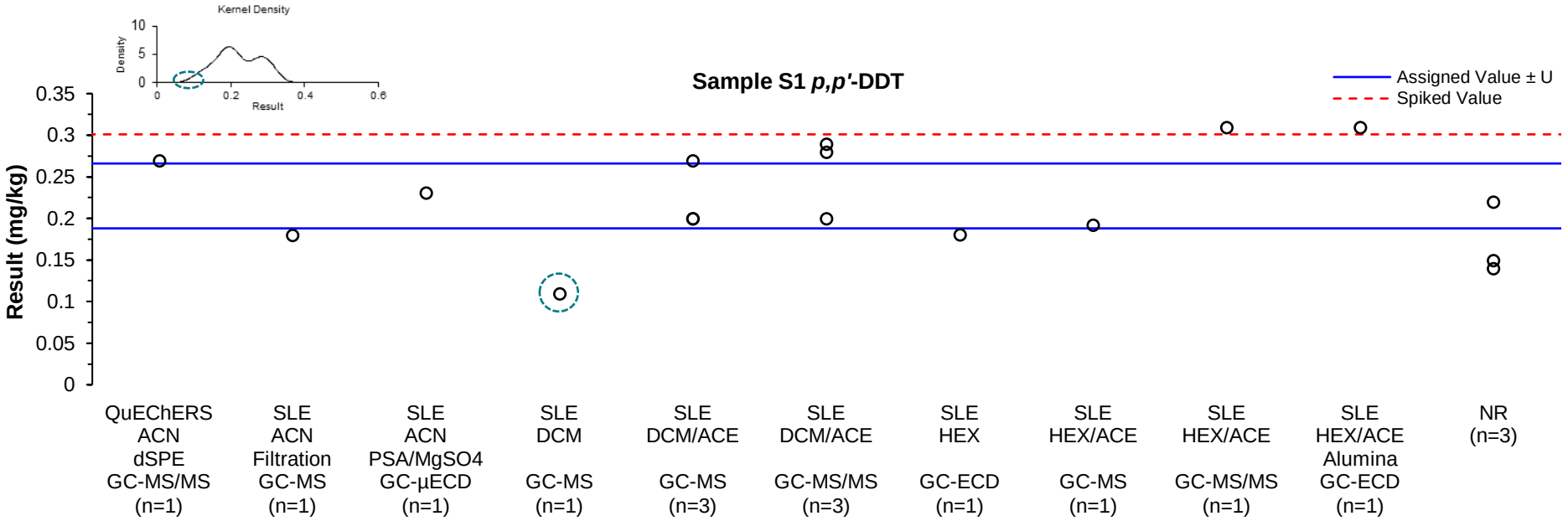


Figure 17 Sample S1 *p,p*'-DDT Results vs Methodology

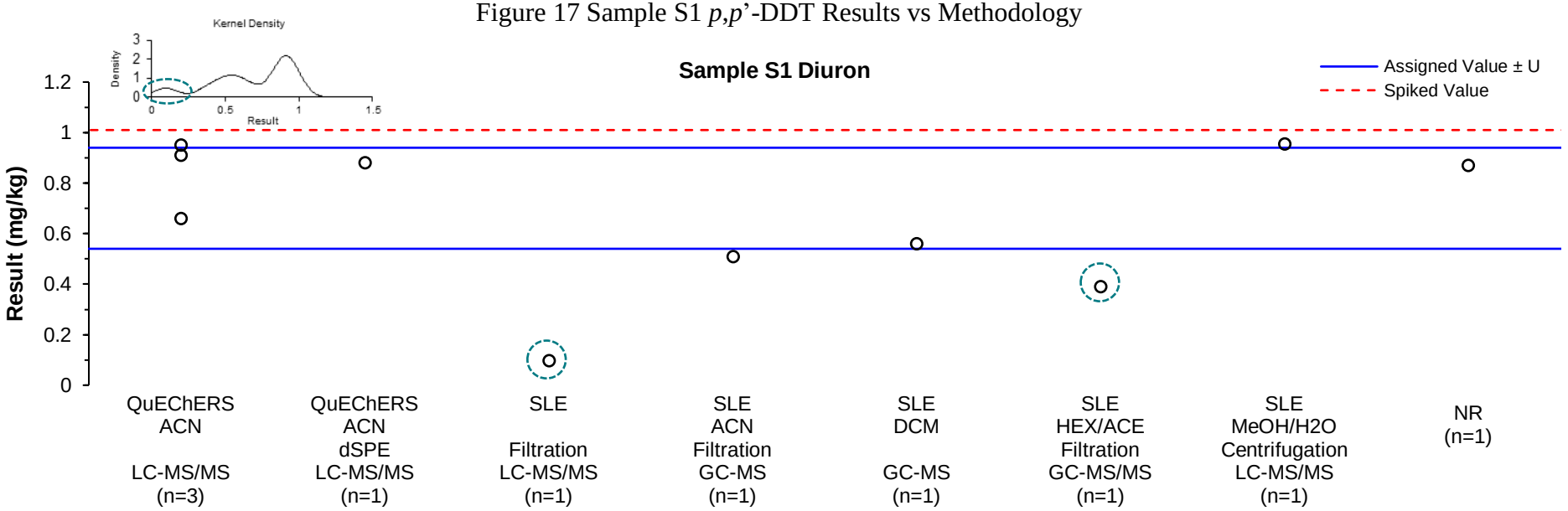


Figure 18 Sample S1 Diuron Results vs Methodology

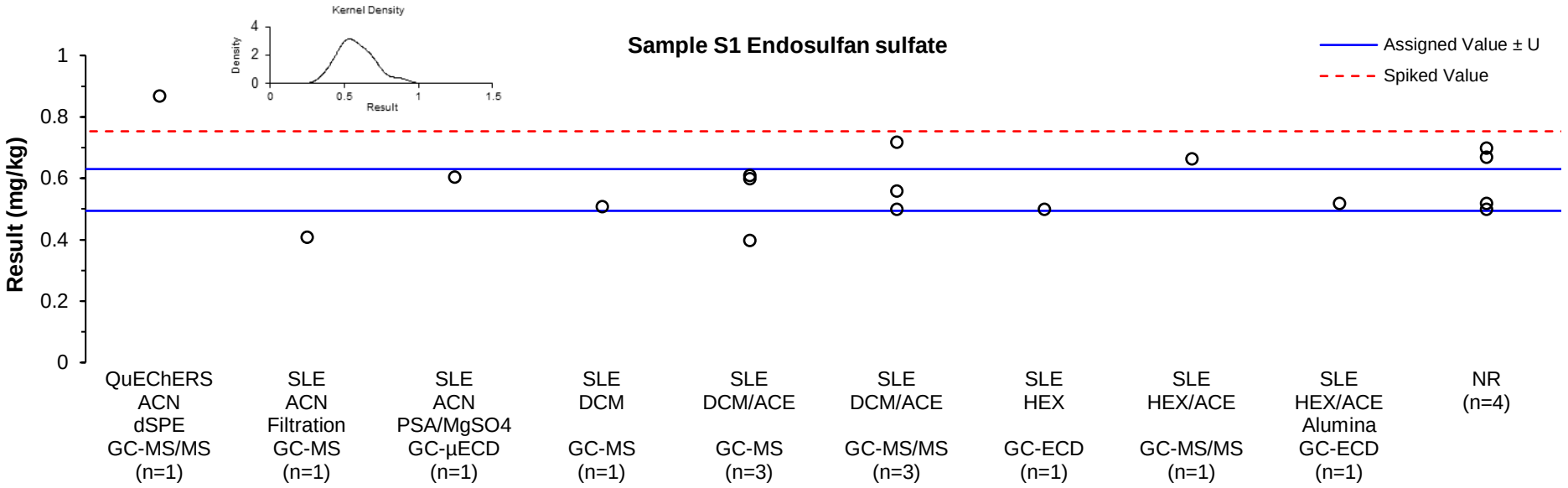


Figure 19 Sample S1 Endosulfan Sulfate Results vs Methodology

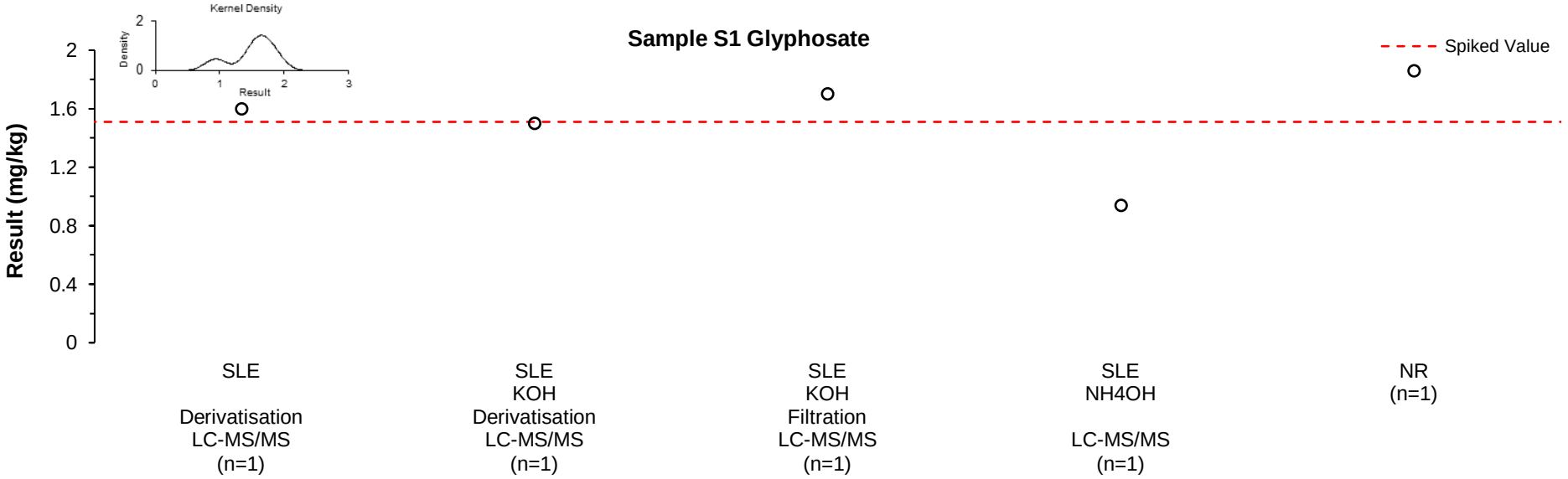


Figure 20 Sample S1 Glyphosate Results vs Methodology

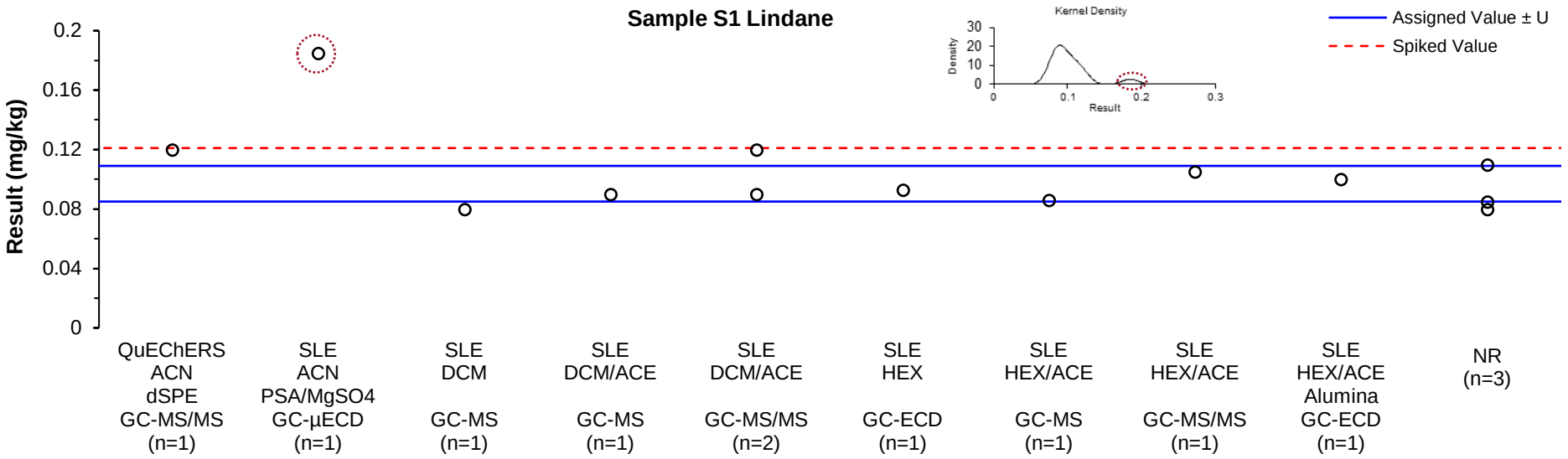


Figure 21 Sample S1 Lindane Results vs Methodology

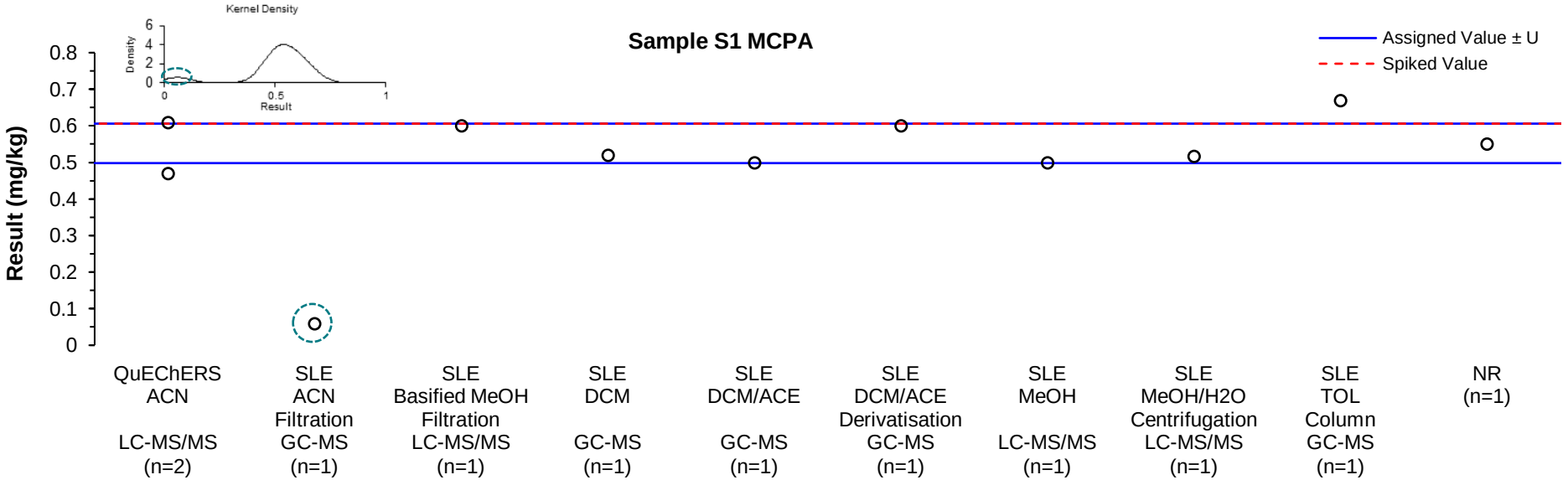


Figure 22 Sample S1 MCPA Results vs Methodology

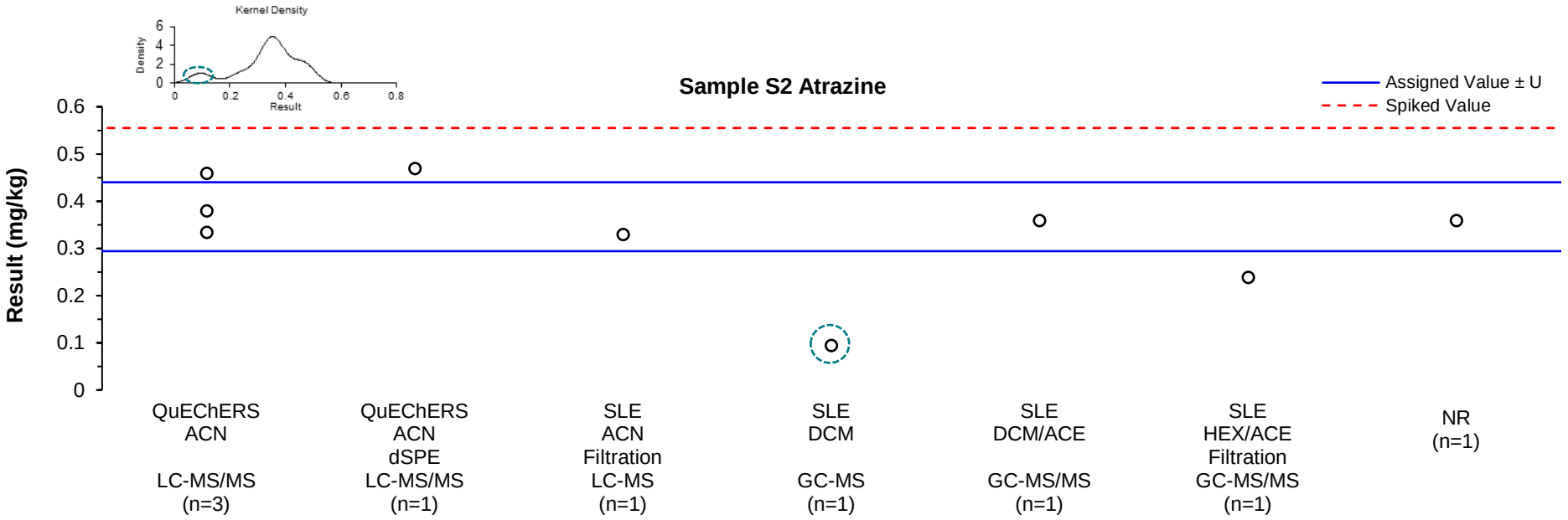


Figure 23 Sample S2 Atrazine Results vs Methodology

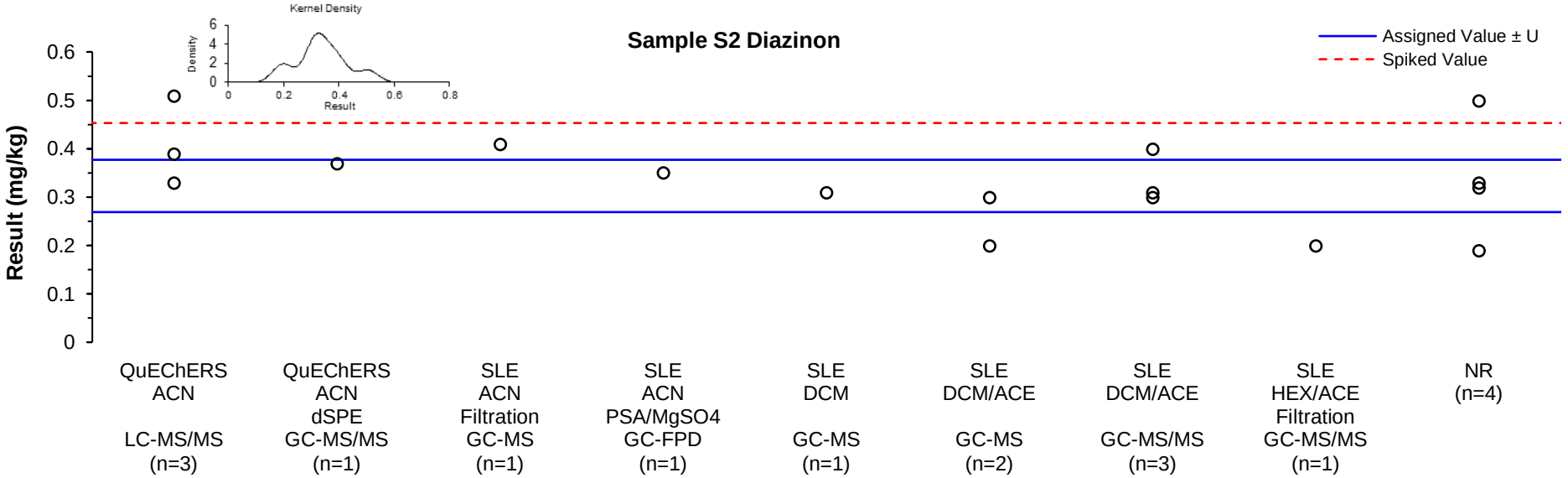


Figure 24 Sample S2 Diazinon Results vs Methodology

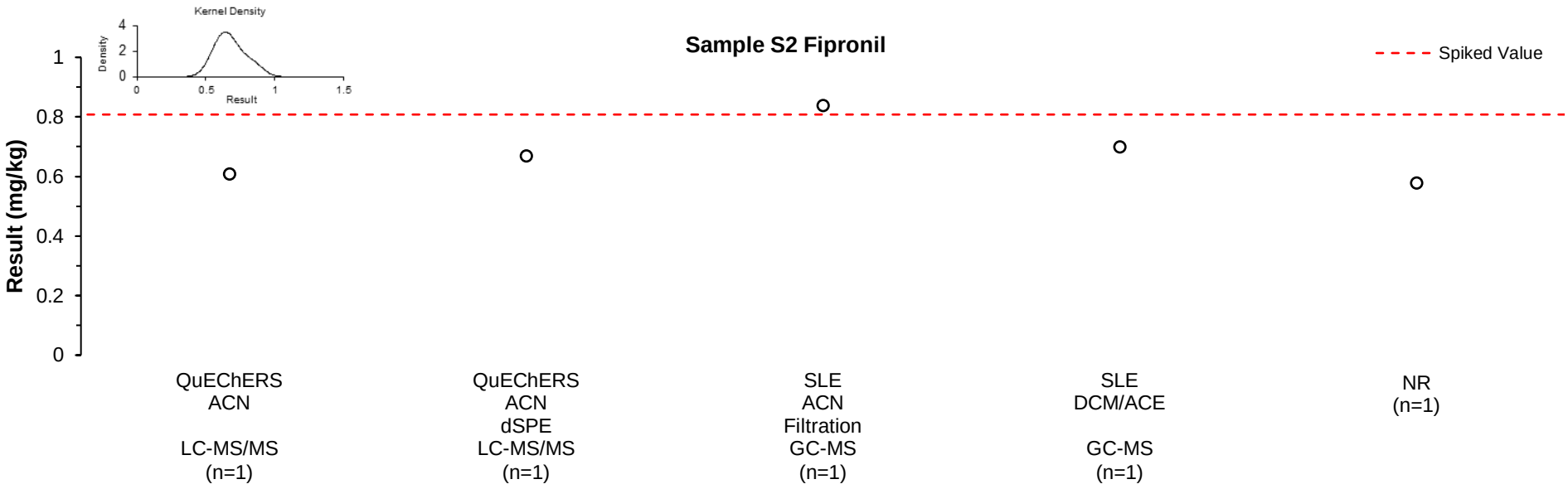


Figure 25 Sample S2 Fipronil Results vs Methodology

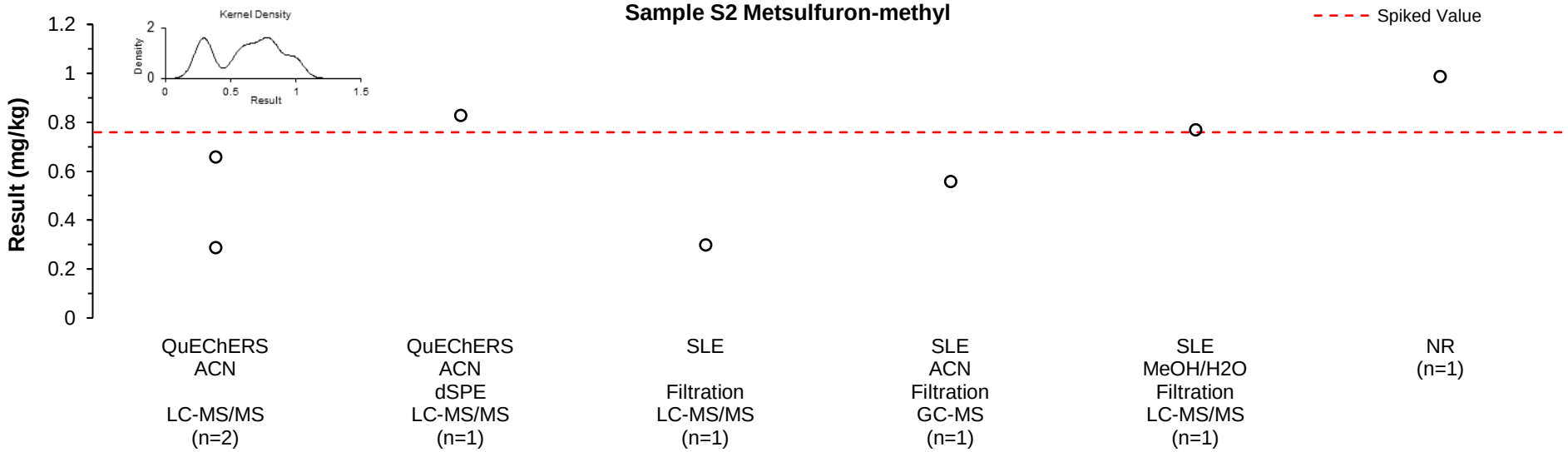


Figure 26 Sample S2 Metsulfuron-methyl Results vs Methodology

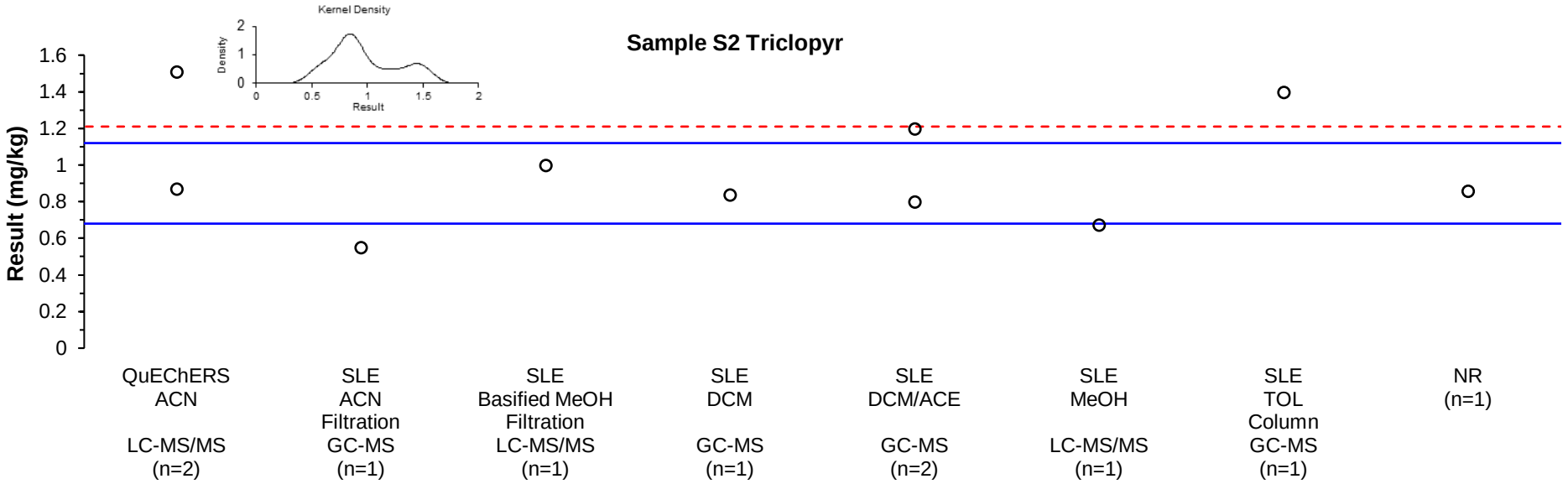


Figure 27 Sample S2 Triclopyr Results vs Methodology

Participants were requested to analyse the samples using their routine test method and to report a single result as they would to a client; that is, corrected for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **2**, **3**, **8**, **9**, **11**, **12**, **13**, **16** and **22** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 56% to 120%. Laboratory **9** reported that they corrected results for recovery.

6.9 Certified Reference Materials

Participants were requested to indicate whether certified standards or matrix reference materials had been used as part of the quality assurance for their analysis. Twelve participants reported using certified standards, one participant reported using matrix reference materials, and one participant reported using both. The following were listed:

- ERA (e.g. CRM727)
- Dr Ehrenstorfer
- o2si
- PM Separations
- Sigma Aldrich (e.g. SQC009, CRM107)
- ISO 17034 standards
- Other pesticide reference standards

These materials may or may not meet the internationally recognised definition of a CRM:

> *'**reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[12]

6.10 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Table 22 and Laboratories **1**, **19** and **22** did not report numeric results for any scored analyte in this study.

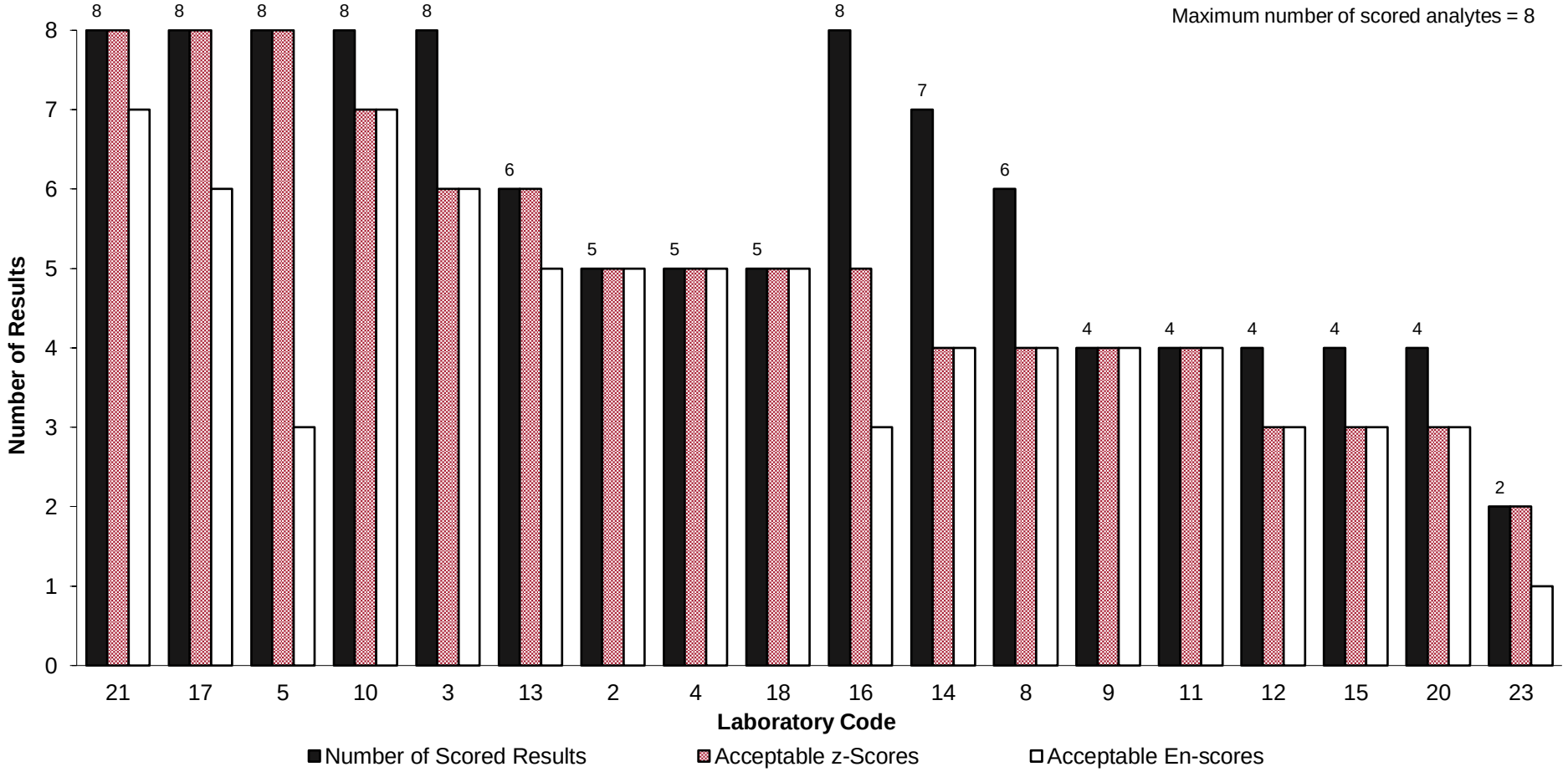
Figure 28.

Table 22 Summary of Participants' Results*

Lab. Code	S1 Diuron	S1 p,p'-DDT	S1 Endosulfan sulfate	S1 Lindane	S1 MCPA	S2 Atrazine	S2 Diazinon	S2 Triclopyr
AV	0.74	0.227	0.562	0.097	0.552	0.367	0.323	0.90
SV	1.01	0.301	0.753	0.121	0.606	0.555	0.453	1.21
1	<0.006	<0.010	<0.010	<0.010	<0.010	<0.006	<0.003	<0.010
2	NT	0.2	0.6	<0.1	0.5	<0.5	0.3	0.8
3	0.56	0.11	0.51	0.08	0.52	0.095	0.31	0.84
4	< 2	0.29	0.72	0.12	< 1	0.36	0.31	NT
5	0.91	0.27	0.61	0.09	0.61	0.46	0.39	1.51
8	0.097	0.2	0.4	<0.1	0.6	<0.5	0.2	1.2
9	0.956	0.1925	NT	0.086	0.517	NT	NT	NT
10	0.87	0.22	0.67	0.11	0.55	0.36	0.19	0.86
11	NT	0.28	0.56	0.09	NT	NT	0.400	NT
12	NT	0.231	0.606	0.185	NT	NR	0.351	NT
13	0.88	0.27	0.87	0.12	NT	0.47	0.37	NT
14	0.51	0.18	0.41	<0.02	0.06	0.33	0.41	0.55
15	NT	0.14	0.52	0.08	NT	NT	0.32	NT
16	0.39	0.31	0.52	0.1	0.67	0.24	0.2	1.4
17	0.95	0.181	0.5	0.093	0.47	0.38	0.51	0.87
18	NT	0.2	0.5	<0.1	0.6	<0.5	0.3	1.0
19	NR	NR	NR	NR	NR	NR	NR	NR
20	NT	0.15	0.5	0.085	NT	NT	0.33	NT

Lab. Code	S1 Diuron	S1 p,p'-DDT	S1 Endosulfan sulfate	S1 Lindane	S1 MCPA	S2 Atrazine	S2 Diazinon	S2 Triclopyr
21	0.66	0.31	0.665	0.105	0.5	0.335	0.33	0.675
22	NT	NT	NT	NT	NT	NT	NT	NT
23	NT	<0.5	0.7	<0.5	NT	NT	0.5	NT

* All results are given in mg/kg. Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value; SV = Spiked Value.



Laboratories **1**, **19** and **22** did not report numeric results for any scored analyte in this study.

Figure 28 Summary of Participants' Performance

6.11 Comparison with Previous Pesticides in Soil PT Studies

A summary of participation and reported results rates in NMIA Pesticides in Soil PT studies over the last 10 studies (2016 – 2025) is presented in Figure 29. The proportion of pesticides being tested for by participants has remained relatively steady over the last few years, though for this study the number of numeric results reported has decreased.

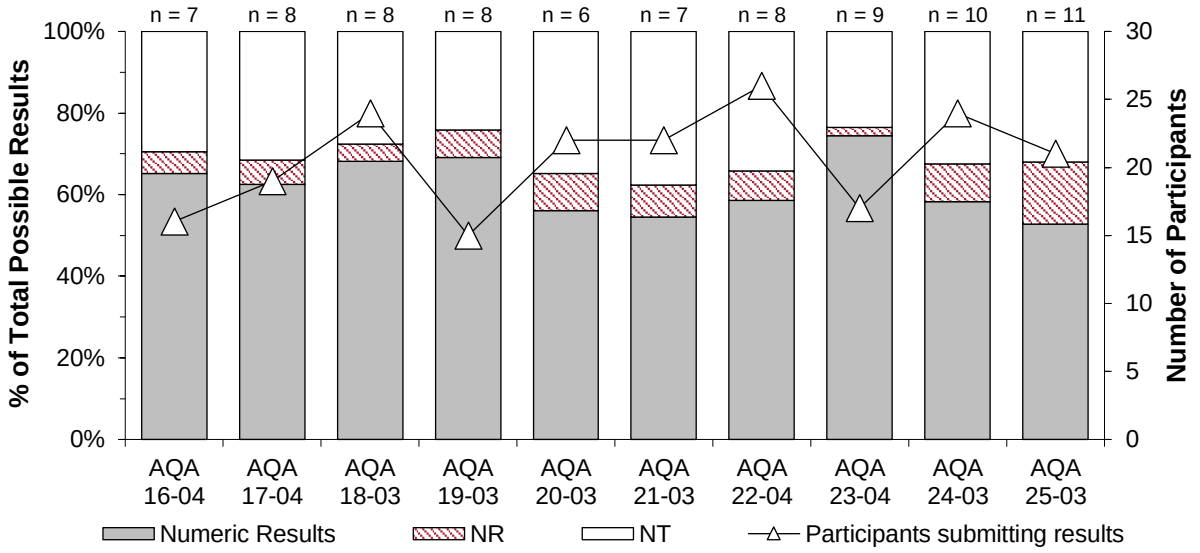


Figure 29 Summary of Participation and Reported Results in Pesticides in Soil PT Studies (n = number of spiked analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores for each study) obtained by participants in NMIA Pesticides in Soil PT studies over the last 10 studies (2016 – 2025) is presented in Figure 30. To enable direct comparison, the target SD for proficiency assessment used to calculate *z*-scores has been kept constant at 15% PCV. Over this period, the average proportion of acceptable *z*-scores and E_n-scores was 88% and 84% respectively.

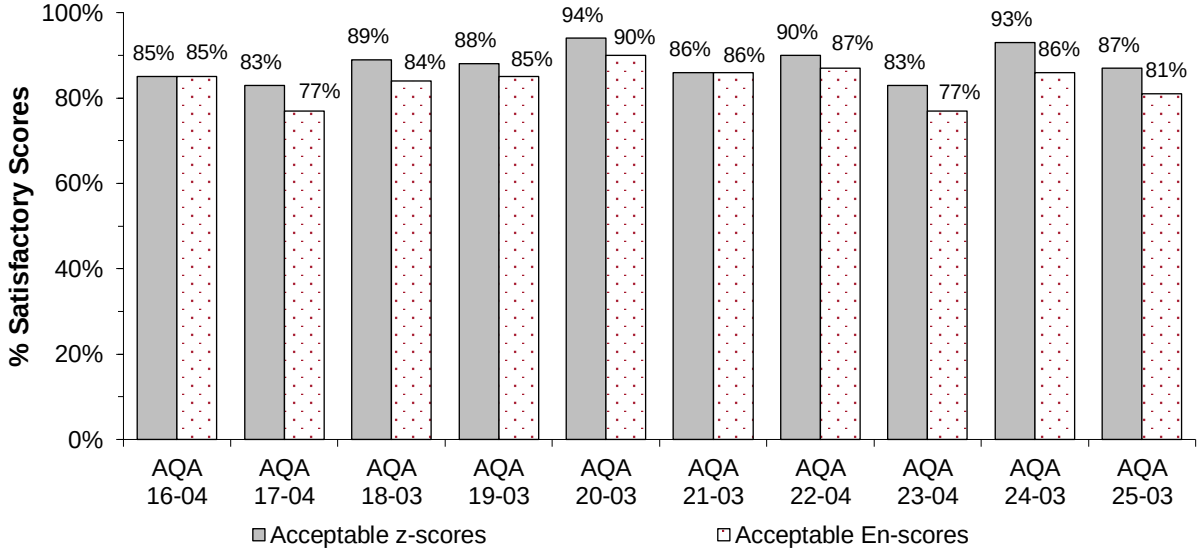


Figure 30 Acceptable *z*-Scores and E_n-scores in Pesticides in Soil PT Studies

Individual performance history reports are emailed to participants at the end of each study; the consideration of *z*-scores over time provides much more useful information than a single score. Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however these should be

interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of *z*-scores on one side of the zero line is an indication of method or laboratory bias.

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties. Figure 31 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2016 – 2025). Over this time period, the vast majority of numeric results were reported with uncertainties (94%), with on average 89% of participants in each study reporting that they were accredited to ISO/IEC 17025. Most participants over this time reported relative expanded uncertainties between 15% and 50%, however around 25% of relative uncertainties were outside this range, and may have been unrealistically small or too large to be fit-for-purpose.

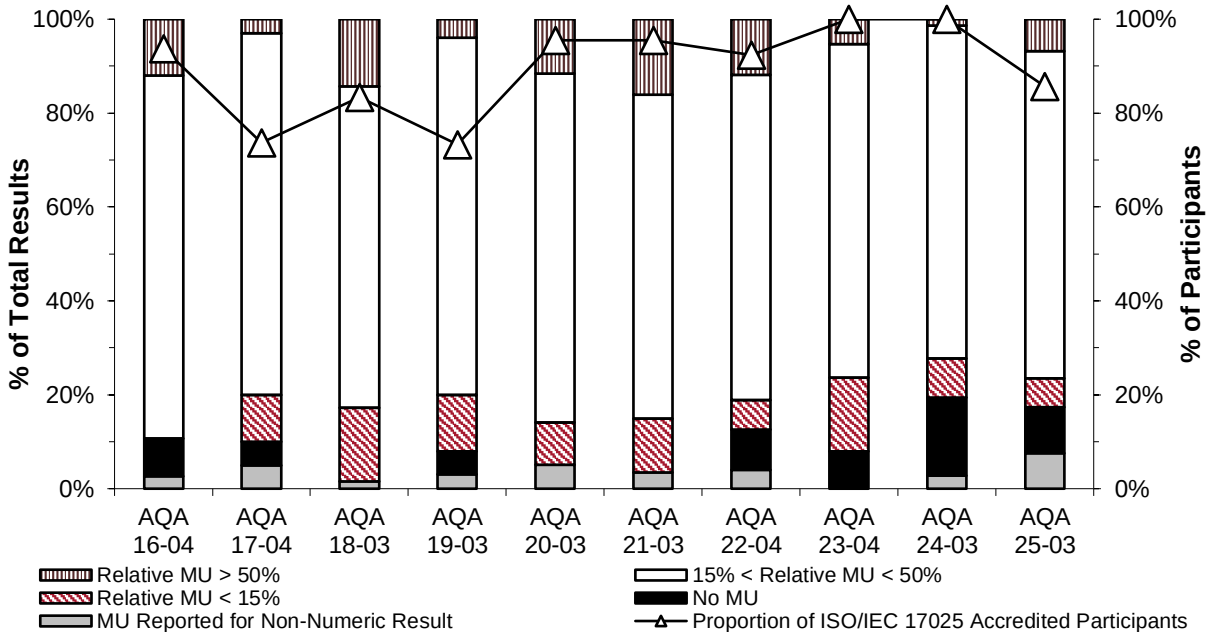


Figure 31 Summary of Participants' Relative Uncertainties for NMIA Pesticides in Soil PT Studies

Diuron was spiked into Sample S1 for this study at a similar level as for previous pesticides in soil PT studies AQA 19-03 and AQA 17-04. Assigned values, spiked values and number of participants submitting numeric results for this analyte in each study are given in Figure 32. The assigned value (based on the consensus of participants' results) has ranged from 65% to 76% of the spiked value. More participants are now reporting numeric results for this analyte, however the variability of participants' results has also increased.

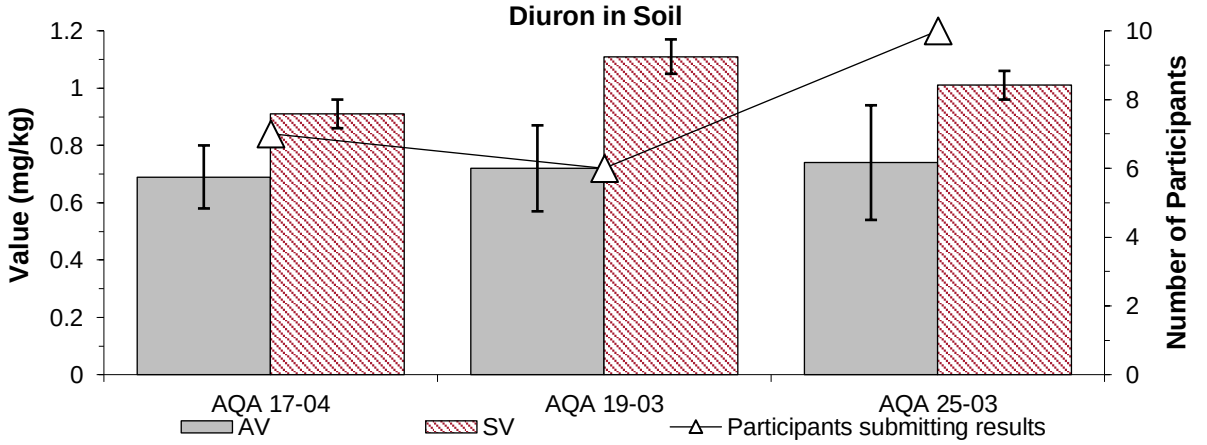


Figure 32 Summary of Diuron in Soil in NMIA Pesticides in Soil PT Studies

7 REFERENCES

Please note that for all undated references, the latest edition of the referenced document (including any amendments) applies.

[1] ISO/IEC 17043, *Conformity assessment – General requirements for the competence of proficiency testing providers*.

[2] NMIA, 2024, *Study Protocol for Proficiency Testing*, viewed June 2025, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] NMIA, 2024, *Chemical Proficiency Testing Statistical Manual*, viewed June 2025, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

[4] Thompson, M., Ellison, S.L.R. & Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, vol. 78, pp. 145-196.

[5] National Environment Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, viewed June 2025, <https://www.legislation.gov.au/F2008B00713/latest/text>.

[6] NMIA, 2016, *Proficiency Test Report AQA 16-04 Pesticides in Soil*.

[7] ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*.

[8] Thompson, M., 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol. 125, pp. 385-386.

[9] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories.*

[10] Eurachem/CITAC Guide GC 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed June 2025, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] US EPA, 2007, *SW-846 Test Method 8081B: Organochlorine Pesticides by Gas Chromatography*, viewed June 2025, <https://www.epa.gov/sites/production/files/2015-12/documents/8081b.pdf>

[12] JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM),* 3rd edition.

APPENDIX 1 SAMPLE PREPARATION

Soil was collected from a farm in New South Wales, Australia.

The soil was dried at 120 °C overnight and then sieved. The fraction of soil between 355–850 µm was retained and used for both samples in the study.

Eleven spike solutions were prepared for this study in acetone and reagent grade water depending on the analyte.

Standards were spiked into the soil material for each sample. The spiked soil was divided up into equal portions of 50 g each, packaged in 65 mL amber glass jars, labelled in fill order and then shrink wrapped.

All samples were stored at 4 °C prior to dispatch.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was conducted for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples.

The results of this study also gave no reason to question the samples' homogeneity. Comparisons of results to bottle number for scored analytes are presented in Figures 33 to 40 (solid blue lines correspond to the assigned value ± U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5, or if that participant was sent more than one container for that sample). No significant fill order trend was observed.

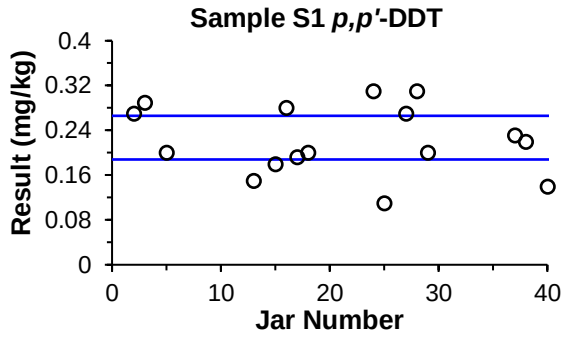


Figure 33 S1 *p,p*'-DDT Results vs Jar Number

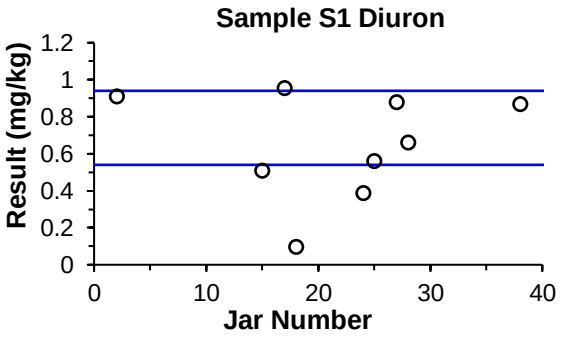


Figure 34 S1 Diuron Results vs Jar Number

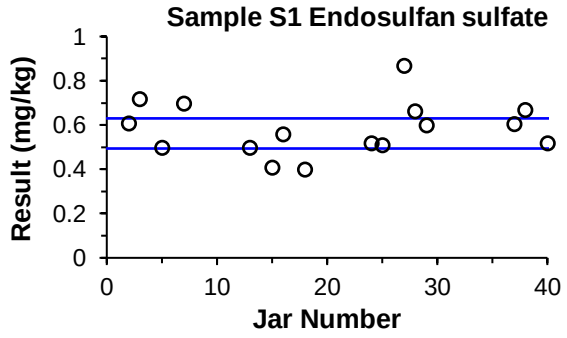


Figure 35 S1 Endosulfan Sulfate Results vs Jar Number

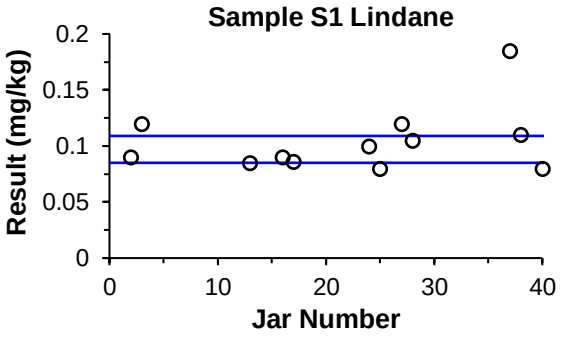


Figure 36 S1 Lindane Results vs Jar Number

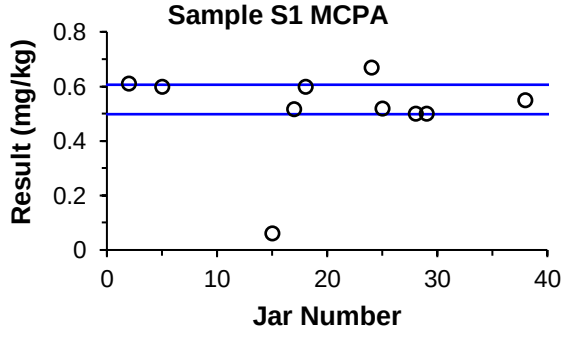


Figure 37 S1 MCPA Results vs Jar Number

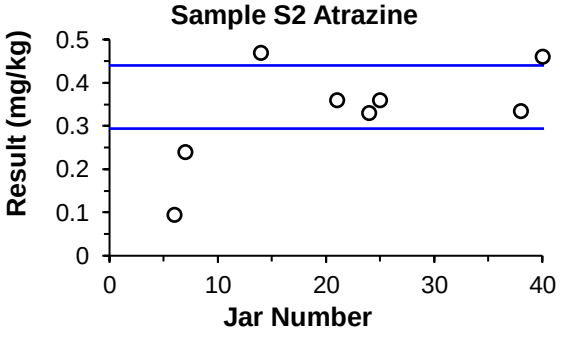


Figure 38 S2 Atrazine Results vs Jar Number

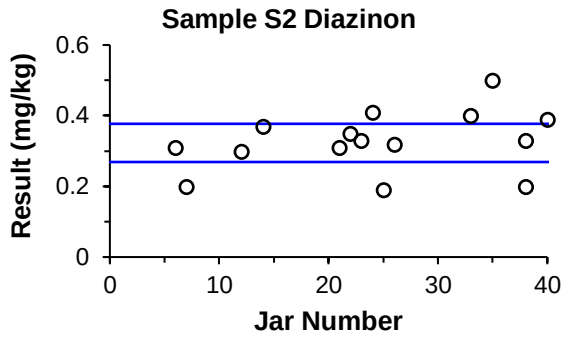


Figure 39 S2 Diazinon Results vs Jar Number

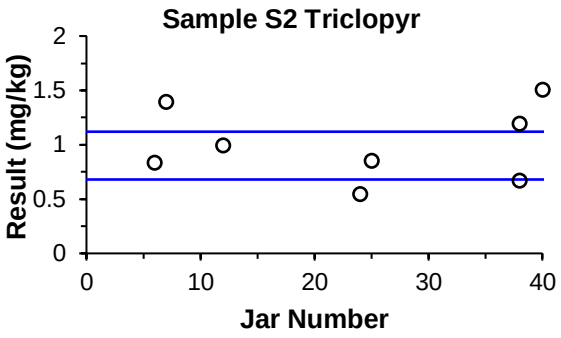


Figure 40 S2 Triclopyr Results vs Jar Number

A2.2 Stability

No stability testing was conducted for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices over a similar time frame. After preparation and before dispatch, the samples were stored in a refrigerator at approximately 4 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

The results of this study also gave no reason to question the samples' transportation stability. Comparisons of results to days spent in transit for scored analytes are presented in Figures 41 to 48 (solid blue lines correspond to the assigned value ± U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5). No significant trend was observed.

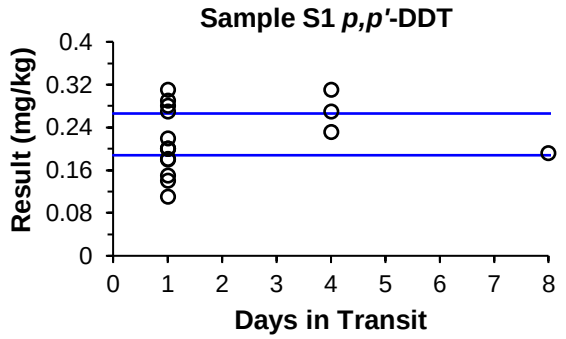


Figure 41 S1 *p,p*'-DDT Results vs Transit Days

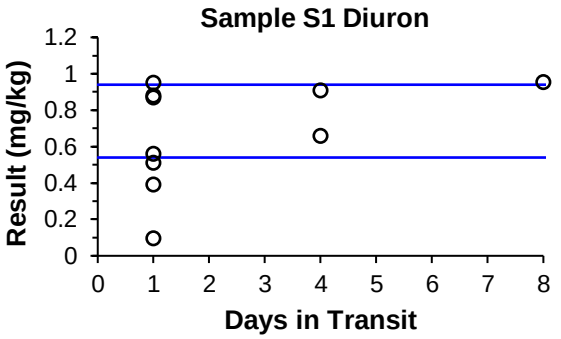


Figure 42 S1 Diuron Results vs Transit Days

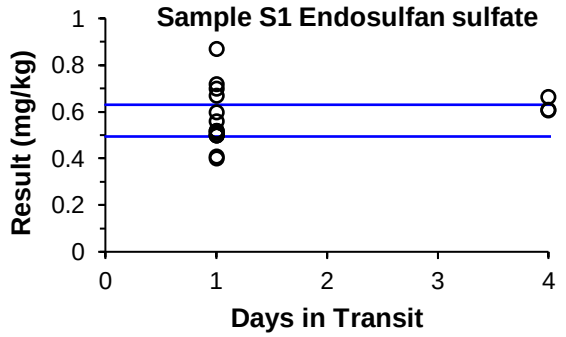


Figure 43 S1 Endosulfan Sulfate Results vs Transit Days

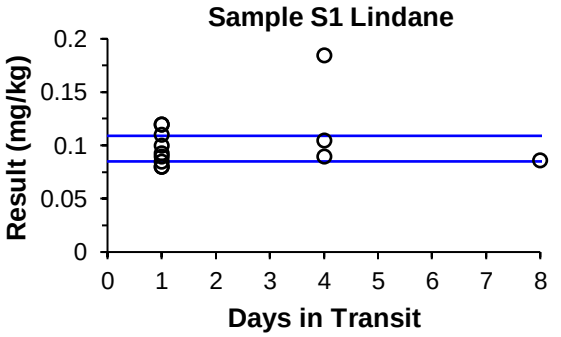


Figure 44 S1 Lindane Results vs Transit Days

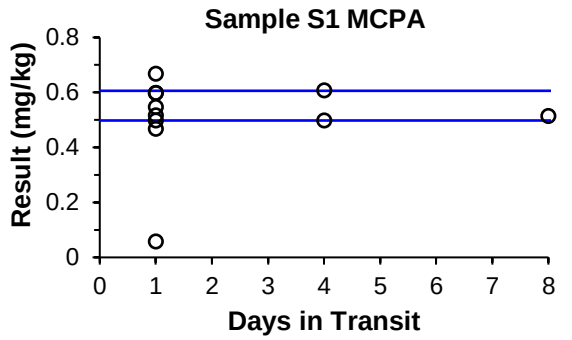


Figure 45 S1 MCPA Results vs Transit Days

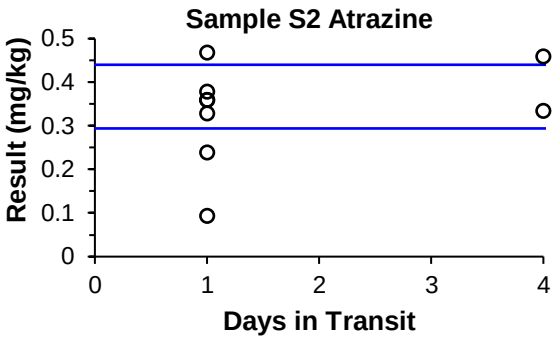


Figure 46 S2 Atrazine Results vs Transit Days

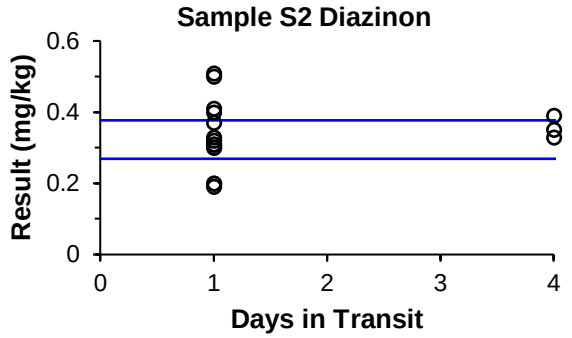


Figure 47 S2 Diazinon Results vs Transit Days

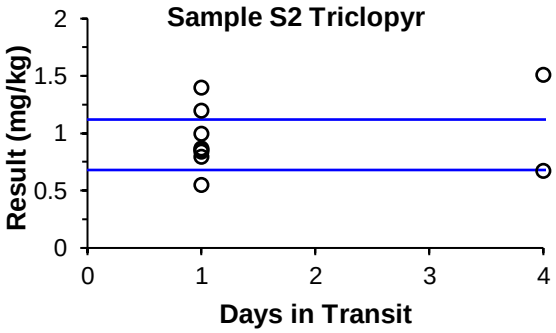


Figure 48 S2 Triclopyr Results vs Transit Days

APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E_n-SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[7] The associated uncertainties were evaluated as according to Equation 4.

$$u_{rob\ av} = \frac{1.25 \times S_{rob\ av}}{\sqrt{p}} \qquad \textit{Equation 4}$$

where:

$u_{rob\ av}$ is the standard uncertainty of the robust average

$S_{rob\ av}$ is the standard deviation of the robust average

p is the number of results

The expanded uncertainty ($U_{rob\ av}$) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in Table 23.

Table 23 Uncertainty of the Robust Average for Sample S2 Atrazine

No. results (p)	9
Robust Average	0.348 mg/kg
$S_{rob\ av}$	0.010 mg/kg
$u_{rob\ av}$	0.042 mg/kg
k	2
$U_{rob\ av}$	0.084 mg/kg

Therefore, the robust average for Sample S2 atrazine is 0.348 ± 0.084 mg/kg.

A3.2 z-Score and E_n-Score Calculations

For each participant's result, a *z*-score and E_n-score are calculated according to Equations 2 and 3 respectively (Section 4).

A worked example is set out below in Table 24.

Table 24 *z*-Score and E_n-Score Calculation for Sample S2 Atrazine Result Reported by Laboratory 3

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target SD	*z*-Score	E_n-Score
0.095 ± 0.03	0.367 ± 0.073	15% as PCV, or: 0.15 × 0.367 = 0.05505 mg/kg	$z = \frac{0.095 - 0.367}{0.05505} = -4.94$	$E_n = \frac{0.095 - 0.367}{\sqrt{0.03^2 + 0.073^2}} = -3.45$

APPENDIX 4 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 25 to 35. Some responses may be modified so that the participant cannot be identified.

Table 25 Methodology – Atrazine

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	9	Sonication	Ethyl acetate	nil	GC-MS
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
5	5	QuEChERS	Acetonitrile Sodium acetate buffer	None	LC-MS/MS
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	NT				
10					
11	NT				
12					
13	10	QuEChERS	ACN	dSPE	LC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	LC-MS
15	NT				
16	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	5	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS
19					
20	NT				
21	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
22	NT				
23	NT				

Table 26 Methodology – *p,p*'-DDT

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	10	Sonication	DCM:Acetone	nil	GC-ECD
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
5	10	Solid-Liquid	DCM/acetone	None	GC-MS
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	5	Solid-Liquid	Aceton:n-hexane 1:1 (V/V)		GC-MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
10					
11	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
12	5	Solid-Liquid	Acetonitrile	PSA,$MgSO_4$	GC-uECD
13	10	QuEChERS	ACN	dSPE	GC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15					
16	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
17	0.1-2 g	Solid-Liquid	HEXANE		GC-ECD
18	5	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS
19					
20					
21	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
22	NT				
23					

Table 27 Methodology – Diazinon

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	9	Sonication	Ethyl acetate	nil	GC-MS
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
5	5	QuEChERS	Acetonitrile Sodium acetate buffer	None	LC-MS/MS
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	NT				
10					
11	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
12	5	Solid-Liquid	Acetonitrile	PSA,$MgSO_4$	GC-FPD
13	10	QuEChERS	ACN	dSPE	GC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15					
16	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	5	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS
19					
20					

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
21	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
22	NT				
23					

Table 28 Methodology – Diuron

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	9	Sonication	Ethyl acetate	nil	GC-MS
2	NT				
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	MEOH	YES	HPLC-DAD
5	5	QuEChERS	Acetonitrile Sodium acetate buffer	None	LC-MS/MS
8	2.5	Solid-Liquid	N/A	Filtration	LC-MS/MS
9	5	Solid-Liquid	MeOH/Water	Centrifugation	LC-MS/MS
10					
11	NT				
12	NT				
13	10	QuEChERS	ACN	dSPE	LC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	NT				
19					
20	NT				
21	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
22	NT				
23	NT				

Table 29 Methodology – Endosulfan Sulfate

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	10	Sonication	DCM:Acetone	nil	GC-ECD
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
5	10	Solid-Liquid	DCM/acetone	None	GC-MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	NT				
10					
11	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
12	5	Solid-Liquid	Acetonitrile	PSA,$MgSO_4$	GC-uECD
13	10	QuEChERS	ACN	dSPE	GC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15					
16	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
17	0.1-2 g	Solid-Liquid	HEXANE		GC-ECD
18	5	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS
19					
20					
21	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
22	NT				
23					

Table 30 Methodology – Fipronil

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	NT				
3	NT				
4	NT				
5	NT				
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	NT				
10					
11	NT				
12	NT				
13	10	QuEChERS	ACN	dSPE	LC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	1	Solid-Liquid	MeOH - H_2O	Filtration	LC-MS/MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	NT				
19					

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
20	NT				
21	NT				
22	NT				
23	NT				

Table 31 Methodology – Glyphosate

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2	NT				
3	NT				
4	NT				
5	NT				
8	1	Solid-Liquid	N/A	Derivatisation	LC-MS/MS
9	1	Solid-Liquid	Water	FMOC-Derivatisation	LC-MS/MS
10					
11	5	Solid-Liquid	Ammonium Hydroxide		LC-MS/MS
12	NT				
13	2.5	Solid-Liquid	0.6N KOH	Organic wash FMOC derivatisation	LC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	1	Solid-Liquid	KOH	Filtration	LC-MS/MS
17	NT				
18	NT				
19					
20	NT				
21	NT				
22					
23	NT				

Table 32 Methodology – Lindane

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	10	Sonication	DCM:Acetone	nil	GC-ECD
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
5	10	Solid-Liquid	DCM/acetone	None	GC-MS
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	5	Solid-Liquid	Aceton:n-hexane 1:1 (V/V)		GC-MS
10					
11	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
12	5	Solid-Liquid	Acetonitrile	PSA,$MgSO_4$	GC-uECD
13	10	QuEChERS	ACN	dSPE	GC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15					
16	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
17	0.1-2 g	Solid-Liquid	HEXANE		GC-ECD
18	5	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS
19					
20					
21	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
22	NT				
23					

Table 33 Methodology – MCPA

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	5	Sonication	MeOH:Formic acid	nil	LC-MS/MS
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	5	Solid-Liquid	MEOH	YES	HPLC-DAD
5	5	QuEChERS	Acetonitrile	None	LC-MS/MS
8	10	Solid-Liquid	DCM/Acetone	Derivatisation	GC-MS
9	5	Solid-Liquid	MeOH/Water	Centrifugation	LC-MS/MS
10					
11	NT				
12	NT				
13	NT				
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	1	Solid-Liquid	Toluene	Column	GC-MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	2.5	Solid-Liquid	Basified Methanol	Filtration	LC-MS/MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
19					
20	NT				
21	2	Solid-Liquid	Methanol	NA	LC-MS/MS
22	NT				
23	NT				

Table 34 Methodology – Metsulfuron-methyl

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2	NT				
3	NT				
4	5	Solid-Liquid	MEOH	YES	HPLC-DAD
5	5	QuEChERS	Acetonitrile	None	LC-MS/MS
8	2.5	Solid-Liquid	N/A	Filtration	LC-MS/MS
9	NT				
10					
11	NT				
12	NT				
13	10	QuEChERS	ACN	dSPE	LC-MS/MS
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	1	Solid-Liquid	MeOH - H_2O	Filtration	LC-MS/MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	NT				
19					
20	NT				
21	NT				
22	NT				
23	NT				

Table 35 Methodology – Triclopyr

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	5	Sonication	MeOH:Formic acid	nil	LC-MS/MS
2	10	Solid-Liquid	DCM:ACE	None	GC-MS
3	3	Solid-Liquid	DCM	None	GC-MS
4	NT				

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
5	5	QuEChERS	Acetonitrile 1% formic in AcN	None	LC-MS/MS
8	10	Solid-Liquid	DCM/Acetone	None	GC-MS
9	NT				
10					
11	NT				
12	NT				
13	NT				
14	50	Solid-Liquid	ACN	Filtration	GC-MS
15	NT				
16	1	Solid-Liquid	Toluene	Column	GC-MS
17	0.1-2 g	QuEChERS	ACETONITRILE		LC-MS/MS
18	2.5	Solid-Liquid	Basified Methanol	Filtration	LC-MS/MS
19					
20	NT				
21	2	Solid-Liquid	Methanol	NA	LC-MS/MS
22	NT				
23	NT				

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ACE	Acetone
ACN	Acetonitrile
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
2,4-D	2,4-Dichlorophenoxyacetic acid
DAD	Diode Array Detection
DCM	Dichloromethane
p,*p*'-DDD	Dichlorodiphenyldichloroethane
p,*p*'-DDE	Dichlorodiphenyldichloroethylene
p,*p*'-DDT	Dichlorodiphenyltrichloroethane
Total DDT	Sum of DDD, DDE and DDT analytes
dSPE	Dispersive Solid Phase Extraction
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
FPD	Flame Photometric Detection
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
HEX	Hexane
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
k	Coverage Factor
LC	Liquid Chromatography
LOR	Limit Of Reporting
Max	Maximum
MCPA	2-Methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty

N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NMIA	National Measurement Institute Australia
NR	Not Reported
NT	Not Tested
PCV	Performance Coefficient of Variation
PSA	Primary-Secondary Amine
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe preparation method
RA	Robust Average
Rec	Recovery
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SS	Spiked Samples
SV	Spiked Value
TOL	Toluene
U	Expanded Uncertainty

END OF REPORT